The background of the slide is a dark, green-tinted photograph of a complex industrial facility, likely a chemical plant. It features multiple levels of metal scaffolding, walkways, and large vertical pipes. The lighting is dim, with some yellowish-green lights visible within the structure. On the far left, there is a solid yellow vertical bar.

A PILOT STUDY OF ENERGY PERFORMANCE LEVELS FOR THE U.S. CHEMICAL INDUSTRY

A PILOT STUDY OF ENERGY PERFORMANCE LEVELS FOR THE U.S. CHEMICAL INDUSTRY

Prepared for
The U.S. Department of Energy's
Office of Industrial Technologies and

Oak Ridge National Laboratory
(Managed by UT-Battelle, LLC for the Department of Energy under contract DE-AC05-
00OR22725)

by BRIDGES to Sustainability
Houston, Texas

June 2001

ACKNOWLEDGEMENTS

This study was carried out by BRIDGES to Sustainability under a subcontract with Oak Ridge National Laboratory which is managed by UT-Battelle, LLC for the Department of Energy under contract DE-AC05-00OR22725. The primary participants from BRIDGES were:

- Earl Beaver, Chief Technical Officer, and Beth Beloff, President, who were the principal investigators, and
- Jeanette Schwarz and Dicksen Tanzil, a post-doctoral student from Rice University.

We would like to thank the many individuals and organizations that contributed to this study, including

- David Huestis and Ron Smith of SRI International for assisting in supplying and interpreting PEP data and providing a detailed review of results,
- David Allen, a professor at the University of Texas who consulted on the project,
- John Carberry of DuPont, David Constable of Glaxo SmithKline, and Joseph Rogers of the American Institute of Chemical Engineers' Center for Waste Reduction Technologies for input on the project, and
- Paul Scheihing of the U.S. Department of Energy's Office of Industrial Technologies and Sharon Robinson of Oak Ridge National Laboratory for their support of the project.

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EXECUTIVE SUMMARY

The Department of Energy's Office of Industrial Technologies (OIT) Chemicals Industry of the Future program's mission is to assist the *Chemical Industry Vision2020 Technology Partnership* in achieving a 30 percent reduction in energy, water and material use, and toxic and pollutant dispersion per unit of output for the major chemical chains and processes by 2020. This is being achieved by supporting collaborative R&D for new emerging chemical process technologies, design of assessment tools, and promoting energy efficiency best practices. *A Pilot Study of Energy Performance Levels for the U.S. Chemical Industry* report is one component of the Chemicals Industry of the Future portfolio of tools developed to assist in meeting Vision2020 goals.

The project summarized in this report was initiated to demonstrate the feasibility of developing a methodology for establishing practical and economical energy improvement targets for the major chemical processes employed in the U.S. The study was scoped to be a pilot project to evaluate a limited range of energy performance levels for a few chemical processes using process flow sheets typically accessible by major chemical companies. The purpose of the project was to evaluate the requirements for and usefulness of methodologies for realistic energy performance evaluations. The results will be used as input into potential future projects to develop user-friendly tools to assist managers in assessing the current performance of their chemical processes and for use in developing energy reduction strategies.

The study estimated actual energy performance levels for five major chemical processes and compared them to a range of possible performance levels that could be achieved through specific process improvements and redesigns that met or surpassed standard capital investment criteria. A base case process configuration for each product was selected, and three successive levels of energy were calculated. These were compared to the theoretical energy requirement for the process.

The definitions of the energy performance levels are given in Table 1. The resulting calculations for five chemical processes are shown in Table 2 and Figure 1. Table 2 compares the energy performance levels for the five products in terms of total energy consumed (net feedstock energy consumed plus net fuel energy consumed) and gives the corresponding percentage reduction in energy consumed from the base processes. Figure 1 shows how the total energy consumption varies as percentages of the base processes. Energy performance calculations were primarily based on data obtained from the Process Economic Program (PEP) Library at SRI International¹.

For the five chemical products studied, Table 2 shows that optimized heat integration can reduce energy consumption from the base case by about ten percent, while aggressive process redesign can reduce energy consumption from 10 to over 50 percent. The options for process redesign that resulted in the most significant reductions in energy use involved improved reaction systems, including improvements in catalysts and types of reactors, and the addition of reaction stages. All five of the processes involve exothermic

reactions. For the theoretical case, the feedstock energy consumed in the chemical reaction (the heat of reaction) is exported as fuel energy, and the total energy consumed is zero. All of the processes, however, are consumers of both feedstock energy and fuel energy. Product recovery and purification are generally the large fuel energy consumers in these processes.

Although this project was scoped to focus on the energy efficiency of chemical processes, it is important to consider the impacts of energy reducing process alternatives on other decision-making factors. A cursory evaluation of the effect of energy reduction alternatives on other sustainability metrics was completed. Figure 2 shows how the sustainability metrics for energy intensity, material intensity, water consumption and greenhouse gases vary with the energy performance levels for maleic anhydride. The levels show reductions in greenhouse gases and water consumption with reductions in energy intensity. The metrics for process redesign, however, indicate that the improvements in the energy metric come at the expense of an increase in material intensity. Future efforts in this area will need to include how to address such trade-offs.

The data in this report are the results of a study performed by BRIDGES to Sustainability (BRIDGES) under a subcontract with Oak Ridge National Laboratory (ORNL), which is managed by UT-Battelle, LLC for the Department of Energy. The study was scoped to be a pilot project for evaluating the feasibility of developing methodologies to determine realistic energy performance levels for a limited number of chemical processes. OIT, ORNL, and BRIDGES recognize that the results of the pilot project are limited by the methodology used for making energy efficiency calculations, the data used in the process evaluations, and the number of process alternatives which were evaluated. The report does not intend to cover an exhaustive review of all viable alternatives for heat integration strategies and viable process redesign alternatives. For example, the heat integration evaluations only included product specific process improvements; additional energy savings on the order of 15% could likely be obtained by improving equipment such as motors², pumps, process heaters, compressors, and steam generators. In addition, more in-depth evaluations of metrics other than energy efficiency are also needed to allow good decision making for process changes.

Although limited in scope, this study has shown that it is feasible to develop methodologies for determining energy performance levels that could be used by managers in energy reduction strategies. The results from this study will be evaluated to direct the scope of future OIT efforts, which may include additional and/or alternative chemical processes, more in-depth heat integration and process redesign studies, and additional metrics and methodology development.

Table 1. Energy Performance Level Definitions

<p>Level 0: Base Case</p> <p>Level 0 energy performance represents the energy requirements for an unimproved baseline process. The energy produced by a process and recovered, such as steam produced from the heat of reaction, was credited in Level 0 calculations. No other energy savings systems, such as heat integration or heat pumps, were included in the base process.</p>
<p>Level 1: Benchmarked Heat Integration</p> <p>Level 1 energy performance accounts for limited energy savings improvements that are included in the PEP reports' process flowsheet for the base case. These improvements may include heat exchanger networks, improved solvents, and incorporation of power generation.</p>
<p>Level 2: Optimum Heat Integration</p> <p>Level 2 energy performance represents an optimized heat integration flowsheet for the baseline process. It includes improvements identified in the PEP flowsheet (Level 1) plus additional improvements such as additional heat exchanger networks, heat pumps, or changes in process conditions that enable further heat integration. The basic aspects of the process (feedstocks used, the type of reaction and catalyst used, and the separation processes employed) are those found in the base case.</p>
<p>Level 3: Process Redesign</p> <p>Level 3 energy performance involves process redesign to improve energy efficiency. Process redesign uses the same reaction chemistry as the base case, but can reflect process changes such as changes in feedstock (e.g. pure oxygen instead of air), improved catalysts, different process configurations, or alternate separation techniques.</p>
<p>Level 4: Theoretical Energy Requirement</p> <p>Level 4 is the theoretical energy required for the reaction calculated from the change in enthalpy of the reacting system at standard conditions. Level 4 is calculated for the reaction used in the base case, based on 100 percent conversion and 100 percent selectivity to the product.</p>

Table 2. Energy Performance Level Estimates (total energy consumed in BTU/lb product and percent reduction from the base case)

Product	Base Case	Benchmarked Heat Integration	Optimum Heat Integration	Process Redesign	Theoretical
Acetic Acid	3,625 0%	3,625 0%	3,584 1%	3,293 9%	0 100%
Acetic Anhydride	2,785 0%	2,770 1%	2,450 12%	2,217 20%	0 100%
Maleic Anhydride	15,792 0%	13,005 18%	12,330 22%	7,389 53%	0 100%
Terephthalic Acid	11,319 0%	10,038 11%	10,038 11%	7,818 31%	0 100%
Caprolactam	35,805 0%	35,805 0%	33,184 7%	23,501 34%	0 100%

Figure 1. Energy Performance Levels (percentage of total energy consumed compared to the base case)

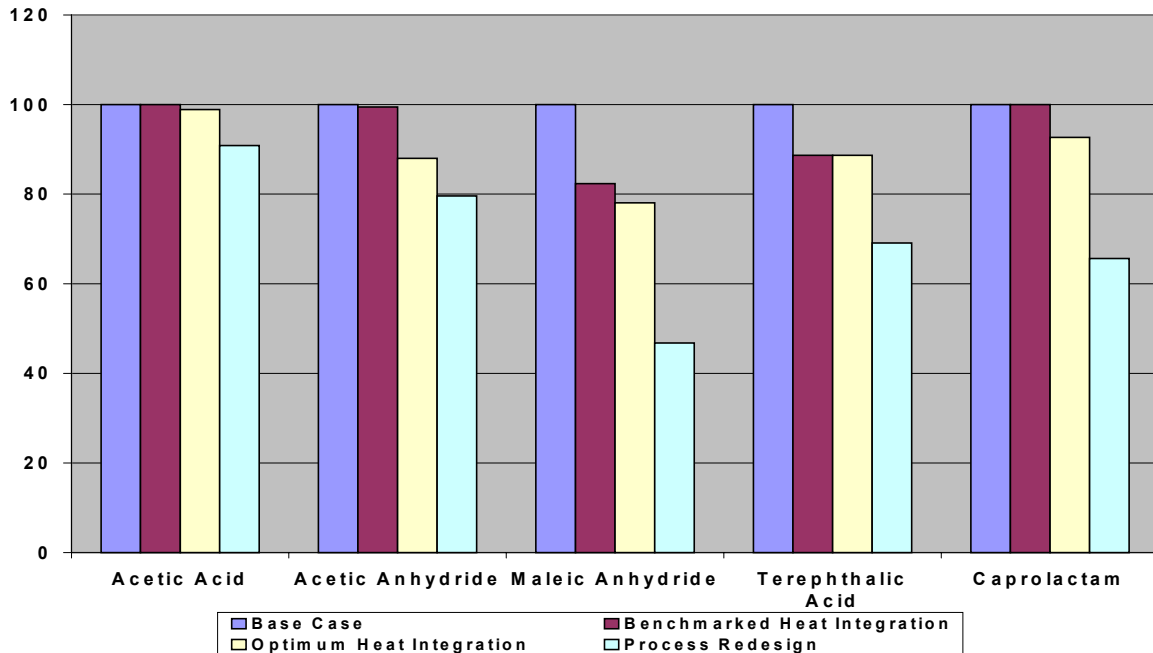
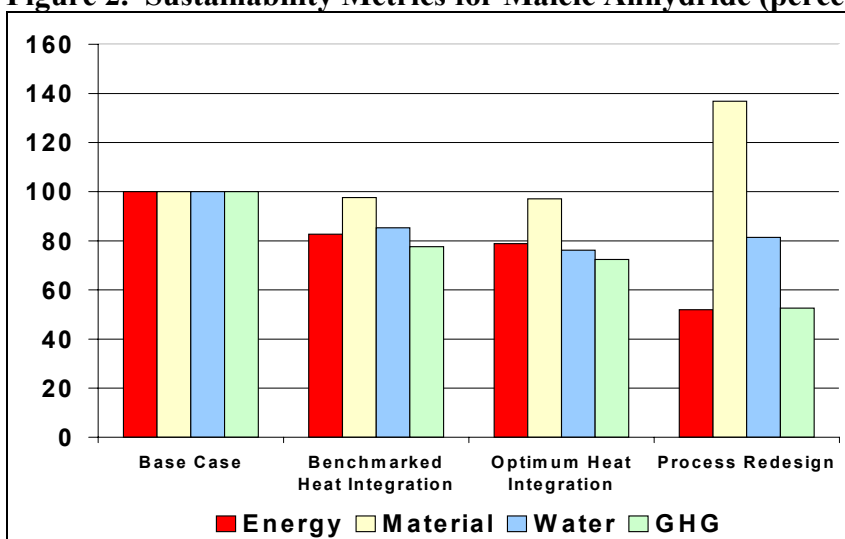


Figure 2. Sustainability Metrics for Maleic Anhydride (percentage of the base case)



1. INTRODUCTION

1.1 Background

The chemical industry faces challenges to advance research and development, maintain global competitiveness, and improve energy and environmental performance. In 1996, chemical industry leaders articulated a long-term vision for the industry, its markets, and its technology in *Technology Vision 2020 – The U.S. Chemical Industry*.³ To achieve the vision, the U.S. chemical industry leaders and the U.S. Department of Energy's (DOE's) Office of Industrial Technologies (OIT) agreed to align resources to meet the industry's long-term R&D needs. The resulting program, established by the OIT Chemicals Industry of the Future team, has a mission to assist the *Chemical Industry Vision2020 Technology Partnership* in achieving a 30 percent reduction in energy, water and material use, and toxic and pollutant dispersion per unit of output for the major chemical chains and processes by 2020 (For more information, visit www.chemicalvision2020.org). This is being achieved by supporting collaborative/innovative R&D to develop new emerging chemical process technologies, design assessment tools/methodologies, and promoting energy efficiency best practices (For more information, visit <http://www.oit.doe.gov/chemicals/>). A *Pilot Study of Energy Performance Levels for the U.S. Chemical Industry* report is one component of the Chemicals Industry of the Future portfolio of tools to assist in meeting Vision2020 goals.

The Chemicals Industry of the Future has developed a partnership with the American Institute of Chemical Engineers (AIChE) to develop and implement tools and methodologies that can drive improvements in operational efficiency as a means of meeting the above reduction goals. These include a suite of sustainability metrics to gauge operational effectiveness as well as related tools and methodologies and best practices programs. The OIT has developed *Energy and Environmental Profile for the U.S. Chemical Industry*⁴ to provide baseline data for major chemical processes. The OIT Best Practices plant-wide assessments program helps chemical manufacturers develop a comprehensive strategy to increase efficiency, reduce emissions, and boost productivity through existing technologies (for more information see www.oit.doe.gov/bestpractices). The AIChE has developed a range of technology and management tools supporting Responsible Care®, sustainable growth and environmental stewardship. These include a total cost assessment methodology that allows companies to include life-cycle environmental, health, and safety costs in decision making, sustainability metrics, and green chemistry/technology guides (for more information see www.aiche.org/cwrt). The information in this document compliments other AIChE and OIT tools by evaluating the energy efficiency of chemical industry process options.

The purpose of this study was to demonstrate the feasibility of developing a methodology for establishing practical and economical energy improvement targets for the major chemical processes employed in the US. The work was performed by BRIDGES

(www.bridgestos.org) under a subcontract with Oak Ridge National Laboratory which is managed by UT-Battelle, LLC for the Department of Energy.

A Pilot Study of Energy Performance Levels for the U.S. Chemical Industry builds on a prior study supported by OIT and undertaken by the AIChE's Center for Waste Reduction Technologies (CWRT) through a subcontract with BRIDGES. The CWRT project developed benchmark values for the following five key sustainability metrics for 50 top chemical processes and some key supply chains: materials consumption, energy use, water use, toxic dispersion, and pollutant dispersion. The results are summarized in *Sustainability Metrics for Chemical Processes and Product Chains*⁵. The CWRT project had a secondary objective of developing indicators for intangible societal costs of the effects and impacts of industrial operations; this work has been summarized in *Evaluation of Societal Costs: Odors and Eutrophication*⁶. The present study builds on the above benchmarking work by identifying energy savings associated with potential process flowsheet improvements for five of the chemical manufacturing processes evaluated in the earlier study.

1.2 Project Objectives

The Chemicals Industry of the Future program is supporting industry in developing metric tools to assist in the selection and assessment of projects that can contribute to meeting energy reduction goals for major chemical chains and processes. Information is needed to allow funding agencies, company management, and engineering staff to evaluate the usefulness of potential process development and improvement efforts, track progress towards performance targets, and facilitate meaningful comparisons of energy use across the chemical industry. The goal is to develop information needed to identify where best practice programs and technology development efforts should be focused for an individual company and industry wide efforts. Through a process of comparing energy efficiencies of alternative technologies with existing practices, one should be able to determine which energy reduction strategies have the maximum potential energy savings, what data and resources are needed to estimate them, and which approaches would be of most use.

One step required in developing these tools is to identify the energy efficiency of existing chemical manufacturing processes and the potential for improving them through process design improvements that meet typical investment hurdles employed by industry. This study was scoped to be a pilot project for evaluating the feasibility of developing methodologies to determine realistic energy performance levels for a limited number of chemical processes. The purpose of the project was to evaluate the requirements for and usefulness of methodologies for realistic energy performance evaluations. The results will be used as input into potential future projects to develop user-friendly tools to assist managers in assessing the current performance of their chemical processes and for use in developing energy reduction strategies.

1.3 Organization of the Report

Several tasks were involved in the development of this project. Various energy performance levels were defined, and criteria were developed for selecting the process improvements to be evaluated in the study. These processes are described in the Methodology Development section of the report.

The methodology was applied to five major chemical processes to calculate the various energy performance estimates. The results are summarized in the Energy Performance Results section of this report.

Although this project focused on the energy efficiency of chemical processes, it is important to consider the impacts of energy reducing process alternatives on other decision-making factors. A cursory evaluation of the effect of energy reduction alternatives on other sustainability metrics was included in the study. Similarly, the relationship between energy intensity and product selling price was evaluated. The results are summarized in the Other Metrics section of the report.

The application of the methodology developed in this study is discussed in the Use of Methodology section.

2. METHODOLOGY DEVELOPMENT

Development of a methodology for determining energy performance levels for chemical processes involved the following major steps:

- Identifying data sources,
- Defining the energy performance levels,
- Developing a method for calculating the energy requirements for each chemical process, and
- Defining the criteria for selecting process configurations for the energy performance evaluations.

Each of these steps is discussed in detail below.

2.1 Data Sources

The work presented here builds on *Sustainability Metrics for Chemical Processes and Product Chains*⁵, in which benchmark sustainability metrics were calculated for 50 major chemical products. Five core sustainability metrics were calculated in this study: material intensity, energy intensity, water consumption, toxics dispersion and pollutants dispersion. Emission of greenhouse gases, a complementary metric in the category of pollutants dispersion, was also determined. The present study builds on the sustainability metrics effort by identifying energy savings associated with potential process flowsheet alternatives to the benchmarked chemical manufacturing processes.

The data for calculating energy consumption were primarily obtained from the Process Economic Program (PEP) Library at SRI International¹. Other sources of information include process simulation programs, the TEAMTM (Tools for Environmental Analysis and Management) software, patents, journals and engineering texts. The PEP reports were selected as the primary reference for this pilot project because they represent process flow sheets that are typically accessible by major chemical companies. Additional sources of process flow sheets and data may be evaluated in future efforts.

The PEP library contains detailed process design and economic information for the production of many major chemicals, often with multiple processing options. The PEP reports contain technical reviews of processes and process design information, including process flow diagrams and stream compositions. Major equipment lists, raw material and utility requirements, capital and operating cost estimates, and the industry status of the product and process are contained in the reports. SRI develops process designs and economics on the basis of information openly available from patents, literature, and communication with industry. A process design may be based on a patent assigned to a particular company but does not necessarily represent a process used by that company or offered by a licensor. The multiple PEP process designs for the manufacture of a given

product, particularly designs that have been developed on the basis of recent patents, were used in evaluating process redesign options.

TEAMTM is a registered trademark of the Ecobilan Group. The TEAMTM software is designed for modeling product life cycles and determining the environmental impacts associated with them. The software is equipped with several hundred modules for generic industrial processes, which form the building blocks of the user-designed life cycle analyses.

2.2 Energy Performance Levels

A critical step in the development of the methodology was to define a series of energy performance levels that would provide manufacturers with a useful guide for setting targets for energy improvements. Five levels of energy requirements were established and are described in detail in Table 1.

A base case process configuration for each product was selected and three successive levels of energy improvement were calculated. The final level is the theoretical energy requirement for the process, which is based on the thermodynamic properties of the products and reactants involved in the process chemistry. The five energy performance levels are:

- Level 0: Base Case
- Level 1: Benchmarked Heat Integration
- Level 2: Optimum Heat Integration
- Level 3: Process Redesign
- Level 4: Theoretical Energy Requirements

A process design that is available in the PEP Library was chosen for Level 0, the base process, for the five products evaluated. The base processes were selected to represent a process configuration that would be commonly used for the manufacture of the product in the U.S. The energy produced by a process and recovered, such as steam produced from the heat of reaction, was credited in Level 0 calculations. No other energy savings systems, such as heat integration or heat pumps, were included in the base process.

Levels 1-3 are successive levels of improvement in energy efficiency from the base case. Levels 1 and 2 represented improvements in energy efficiency that can be made primarily by heat integration. Level 1, the benchmarked heat integration case, included the heat integration systems included in the PEP flowsheets for the baseline flowsheet. These improvements included in PEP flowsheets were heat exchanger networks, improved solvents, and/or incorporation of power generation. Level 1 serves as a reference value, since the PEP reports are known sources of process information. For Level 2, the optimum heat integration case, other energy saving systems, such as process stream heat exchangers and heat pumps, were added to the PEP flowsheet to produce an optimized heat integrated system. The basic aspects of the process (feedstocks used, the type of reaction and catalyst used, and the separation processes employed) did not change for

Levels 1 and 2. Level 3, the process redesign case, energy requirements reflected further improvements in energy efficiency that can be achieved with a process redesign for manufacturing the product. For Level 3, process configurations reflected such changes as improved catalysts, alternate reaction systems, or alternate separation techniques. Process improvements for Levels 2 and 3 were selected only if they passed both an energy criterion and an economic criterion as discussed in Sections 2.3 and 2.4.

Levels 0 and 4 represented the upper and lower boundaries of energy use for the base process. Level 0 energy requirements were for the unimproved base process and Level 4 represented the theoretical energy required to produce the product based on the thermodynamic properties of the chemical reactants and products.

2.3 Energy Requirements for Chemical Processes

The definitions used to calculate the energy requirements of each chemical process were established since energy criteria were needed to choose the most efficient options for optimizing heat integration (Level 2) and for process redesign (Level 3). As well as being a necessary part of the criteria for determining the energy performance levels, the definitions of the energy requirements were important for using the energy performance benchmark levels given in this report to assess the energy performance of actual processes. They build on the energy metric, shown in Figure 3, established in *Sustainability Metrics for Chemical Processes and Product Chains*⁵.

Energy requirements are calculated according to the following definitions:

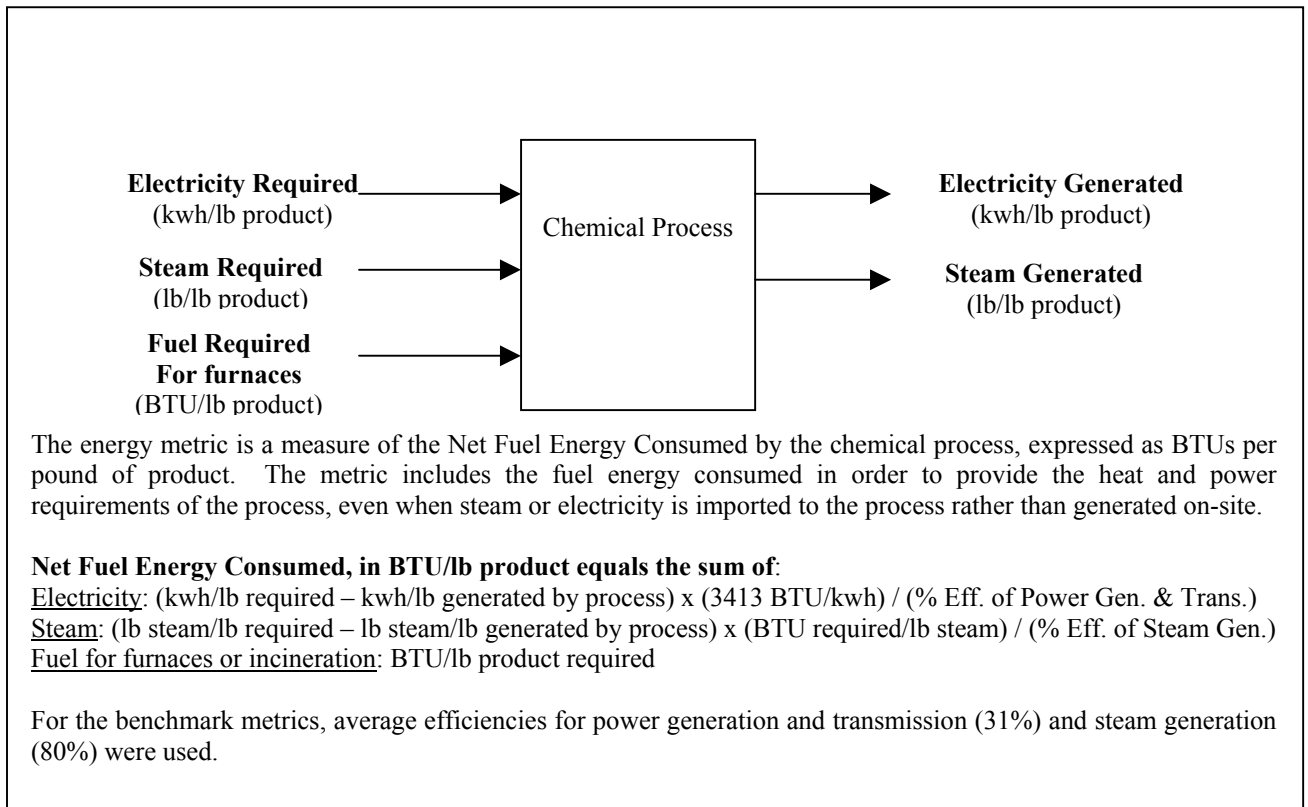
- Net Power and Hot Utility Requirements
- Net Fuel Energy Consumed by the Process
- Total Energy Consumed by the Process
- Total Energy Consumed by the Product Chain

The first three energy requirements were calculated for the chemical processes using PEP process designs and process boundaries. Each process involved the reaction of specified feedstocks, and subsequent recovery operations and purification steps to yield the finished product. Some processes were complex and involved more than one reaction and additional steps for catalyst recovery or waste treatment.

The last energy requirement, total energy consumed in the product chain, includes energy consumption beyond the PEP process boundary. It includes an estimation of the total energy (fuel and feedstock) that has been consumed in the production of the product, beginning with elemental raw materials.

Table 3 summarizes the key elements of the energy requirements, as well as their functions as energy criteria for determining energy performance Levels 2 and 3, and their usefulness in comparing actual processes with the energy performance levels given in this report. The various energy requirements are described in detail below. The criteria for

Figure 3. Energy Intensity Metric



determining energy performance levels mentioned in the discussions below are described in detail in Section 2.4.

Net Power & Hot Utility Requirement

Net power and hot utility requirements consist of the net BTUs per pound of power and hot utility *delivered* to the unit operations of the process. This requirement is the sum of the kwh of electricity (converted to BTUs) required by major equipment (such as compressors, pumps and agitators) and the BTUs of hot utility (steam or heat transfer fluid) delivered to reboilers, heaters, dryers, etc. BTUs of fuel required for incineration or furnaces are also included in net power and hot utility requirements. Credit is given for electricity generated by the process and for heat that can be delivered by steam generated by the process.

Net power and hot utility requirements are useful for comparing the energy requirements of an actual process with the energy performance levels; however, this measurement is not used as a criterion in determining energy performance levels.

Table 3. Energy Requirements for Energy Performance Calculations

Net Power & Hot Utility Requirements

- Equals the net energy delivered to the unit operations of the process
- Not applicable as an energy criterion for selecting improvements for Levels 2 or 3.
- Can be used to compare actual process energy requirements with energy performance benchmark levels.

Net Fuel Energy Consumed by Process

- Equals the net energy consumed to provide the power and hot utility requirements for the process (includes the efficiencies of power and steam generation)
- Serves as the energy criterion for selecting Level 2 process improvements
- Serves as the energy criterion for selecting Level 3 process improvements when the quantity and type of feedstock does not change.
- Can be used to compare actual process energy requirements with the energy performance benchmark levels, if the actual process requirements are calculated with the same efficiencies for power and steam generation used in the calculation of the energy performance benchmark levels.

Total Energy Consumed by the Process

- Equals the sum of the net fuel energy and the raw material energy consumed by the process.
- Serves as the energy criterion for selecting Level 3 process improvements when differing quantities of the same feedstock are used.
- Can be used to compare actual process energy requirements with the energy performance levels for alternative process configurations, if the actual process requirements are calculated with the same efficiencies for power and steam generation used in the calculation of the energy performance benchmark levels.

Total Energy Consumed by the Product Chain

- Equals the sum of the total energy consumed by the process and the total energy consumed in the production of the feedstocks.
- Serves as the energy criterion for selecting Level 3 process improvements when differing types of feedstock are used.
- Not recommended for use in comparing actual process energy requirements with the energy performance benchmark levels.

Net Fuel Energy Consumed by the Process

The first criterion used for determining energy performance levels is the net fuel energy consumed by the process. This measurement is identical to the energy intensity metric calculated in *Sustainability Metrics for Chemical Processes and Product Chains*⁵ (see Figure 3) and takes into account the energy needed to *generate* the power and steam needed for the process.

The efficiencies of power and steam generation are important factors in choosing which process improvements result in reduced energy consumption. For the energy performance benchmark levels, as well as for the benchmark sustainability metrics, average values for the efficiencies of steam generation (80%) and electricity generation and transmission (31%) were assumed. Credit is given in terms of fuel equivalents (using the same efficiencies) for steam or electricity that is generated by the process.

The lowest net fuel energy consumed by the process is the energy criterion used for selecting Level 2 improvements. Level 2 improvements involve enhanced heat integration of the base process, which result in reductions in hot utility requirements. Level 2 improvements may also involve expanding a high-pressure gas stream to generate electricity, resulting in reduced net power requirements. Level 2 changes do not involve changes in the type or amounts of feedstocks used in the process.

The lowest net fuel energy consumed by the process is also the energy criterion for selecting the Level 3 process redesign option when the quantity and type of feedstock is not altered from the base process.

Net fuel energy consumed by the process may be used for comparing an actual process with the energy performance benchmark values. However, the energy requirements for the actual process must be calculated with the same efficiencies used for the energy performance calculation. Otherwise the comparison will be difficult to interpret, because it will reflect differences in these efficiencies rather than exclusively in process performance.

Total Energy Consumed by the Process

For Level 3, Process Redesign, the net fuel energy consumed does not always serve as an adequate measure to select the most energy efficiency redesign options. Sometimes, when the chemical reaction is exothermic, an improved value for net fuel energy consumed may actually stem from consuming additional feedstock, rather than from improvements in energy efficiency. When the *quantity of feedstock* is changed, as it often is for a new process design, the energy of the raw materials consumed must also be considered.

Total energy consumed by the process is the sum of the net fuel energy consumed by the process as described above and the raw material energy consumed in the chemical reaction. When two process redesign options use *differing quantities of the same feedstock*, the lowest value for total energy consumed is the energy criterion for selecting the process redesign option.

The total energy consumed by the process may also be used for comparing an actual process with the energy performance benchmark values, if, as discussed above, the same efficiencies are used in the calculation of the net fuel energy consumed.

Total Energy Consumed by the Product Chain

Level 3, Process Redesign, may also involve changing the *type of feedstock* used in the reaction. If this is the case, it becomes necessary to consider the energy requirements of the product chain as well as the process being evaluated. Reducing the energy consumed in one process step at the expense of increasing the energy consumption of the product chain would ultimately be a poor decision.

The total energy consumed by the product chain is an estimate of the total energy consumption (fuel energy and raw material energy) required to produce the product

beginning with elemental raw materials. It is the sum of the total energy consumed in the process as described above and the total energy consumed in feedstock production, beginning with elemental raw materials. When two process redesign options use *different types of feedstocks*, the lowest value for total energy consumed is the energy criterion for selecting the process redesign option.

For the calculations presented in this report, the total energy consumed in feedstock production is estimated using information from the TEAMTM software. The primary energy given for a product in the software database is a measure of the fuel energy required to produce the product plus the feedstock energy consumed (expressed in terms of net calorific value) beginning with elemental raw materials.

The total energy consumed in the product chain is a useful calculation for comparing the energy intensity of different feedstocks. Its use for benchmarking actual processes is not recommended, however, because the life cycle calculation requires numerous steps and assumptions which are difficult to extract from the software, and which could cause the results for any one product to vary considerably.

Calculation of the Energy Requirements

Table 4 lists the data required for calculating energy performance levels, and formulas used for calculating energy performance levels are given in Table 5. All energy requirements are expressed as BTUs per pound of product.

The data listed in Table 4, with the exception of the final item, are usually readily obtained from the flow diagram of the process, facility utilities data and reference texts containing physical and thermodynamic properties. The process data used for the benchmark energy performance levels calculated in this report are obtained from PEP process designs. Average efficiencies are assumed for power and steam generation.

Table 4. Data Required for Calculating Energy Performance Calculations

Process data required:

- Temperatures and heating requirements of unit operations (BTU/hr)
- Kw requirements for major equipment (compressors, pumps, agitators, etc.)
- Lb/hr and pressure of steam generated by process
- Kw of power generated by process
- Product flowrate in lb/hr
- Lb feedstock required per pound of product

Facility data required:

- Efficiency of steam generation
- Efficiency of electricity generation

Thermodynamic data required:

- Standard enthalpies of formation for reactants and products

Additional data required:

- Estimates of energy required to manufacture feedstocks, beginning with elemental raw materials

Table 5. Formulas for Calculating Benchmark Energy Performance Levels

<p>Net Power & Hot Utility Requirements equals the sum of:</p> <p><u>Electricity requirement in BTU/lb</u> = (kw required for major equipment) x (3413 BTU/kwh) / (lb/hr product)</p> <p><u>Hot Utility requirement in BTU/lb</u> = (BTU/hr required for heating) / (lb/hr product)</p> <p><u>Electricity credit in BTU/lb</u> = -(kw generated by process) x (3413 BTU/kwh) / (lb/hr product)</p> <p><u>Hot Utility credit in BTU/lb</u> = -(lbs/hr steam generated by process) x (BTU/lb steam) / (lb/hr product) where BTU/lb steam = heat of vaporization of steam</p>
<p>Net Fuel Energy Consumed by the Process equals the sum of:</p> <p><u>Fuel Energy for Electricity Generation in BTU/lb</u> = (kw required for major equipment) x (11,000 BTU/kwh) / (lb/hr product)</p> <p><u>Fuel Energy for Steam Generation in BTU/lb</u> = (Lbs steam/hr required by process) x (1350 BTU/lb steam) / (lb/hr product) where lbs steam/hr = Σ (BTU/hr required for heating / BTU/lb steam) calculated at each steam pressure</p> <p><u>Fuel Energy for Heat Transfer Fluid in BTU/lb</u> = (BTU/hr required for heating)/0.85/ (lb/hr product)</p> <p><u>Fuel for waste incineration in BTU/lb</u> = (BTU/hr required for heating) / (lb/hr product)</p> <p><u>Fuel Energy Credit in BTU/lb</u> = -(Lbs steam/hr generated by the process) x (1350 BTU/lb steam) / (lb/hr product) + -(kw generated by process) x (11,000 BTU/kwh) / (lb/hr product) All steam generated at 100 psig or greater is credited as fuel energy generated. Steam at pressures less than 100 psig is not credited unless it can be used to meet heating requirements within the process.</p> <p>For the theoretical process, Net Fuel Energy Consumed by the Process = $\Sigma \Delta H^f$ products – $\Sigma \Delta H^f$ reactants for the ideal equation at standard conditions.</p>
<p>Total Energy Consumed by the Process equals the sum of:</p> <p><u>Net Fuel Energy Consumed by the Process in BTU/lb</u> <u>Raw Material Energy Consumed by the Process in BTU/lb</u> = $\Sigma \Delta H^f$ reactants – $\Sigma \Delta H^f$ products at standard conditions For organic oxidation reactions assume excess reactants are converted to CO₂ and water.</p> <p>For the theoretical process, Total Energy Consumed by the Process = 0.</p>
<p>Total Energy Consumed by the Product Chain equals the sum of:</p> <p><u>Total Energy Consumed by the Process in BTU/lb</u> <u>Total Energy Consumed in Feedstock Production in BTU/lb</u> = Energy consumed in the production of feedstocks beginning with elemental raw materials (Estimated from life cycle analysis software using Fuel Energy + Feedstock Energy, where Feedstock Energy equals the net heat of combustion of the feedstocks.)</p> <p>For the theoretical process, Total Energy Consumed by the Product Chain = 0.</p>

Data on the energy required to manufacture the feedstocks were obtained from the TEAMTM life cycle analysis software. In actual practice, this data may be difficult to obtain if feedstocks for the process are purchased from outside suppliers. As explained

above, however, information concerning feedstock process energy is needed only when evaluating different types of feedstocks for the process.

2.4 Energy Performance Level Process Selection Criteria

The last step in developing the methodology for energy performance calculations was defining the criteria for selecting process configurations to be evaluated for the various energy performance levels. The base process was selected to represent the most predominant method for manufacturing the product in the United States, and the Level 1 improvements were determined by the PEP process design for the base process. The selection of the process improvements that make up Levels 2 and 3 required the development of a system for discovering the potential improvement options, and a set of criteria for choosing the best combination of options. Table 6 summarizes the systems developed for evaluating improvements to the base process and the energy and economic criteria used to select the process modifications to represent Levels 2 and 3.

Table 6. Criteria for Selecting Process Configurations for Energy Performance Levels 2 and 3

<p>Level 2: Optimum Heat Integration</p> <p><u>System for evaluating base process for improvements</u></p> <ul style="list-style-type: none"> • Application of Pinch Analysis to discover opportunities for process stream heat exchangers and heat pumps. • Examination of opportunities for generating power by expanding high pressure gas streams <p><u>Energy Criterion</u> Lowest Net Fuel Energy Consumed</p> <p><u>Economic Criterion</u> Payback Period of 3 years or less</p>
<p>Level 3: Process Redesign</p> <p><u>System for evaluating base process for improvements</u> Evaluate modifications in:</p> <ul style="list-style-type: none"> • Material selection • Unit operation design • Process integration and recycle structure • Utility design and fluid handling <p><u>Energy Criteria</u> Lowest Net Fuel Energy Consumed: When quantity and type of feedstocks are the same as the base process Lowest Total Energy Consumed by Process: When type of feedstock is the same, but quantity is different from base process Lowest Total Energy Consumed by Product Chain: When type of feedstock is different from base case</p> <p><u>Economic Criteria</u> Product Value Lower than that of Base Process or References from literature that indicate economic feasibility</p>

Many opportunities exist for improving energy efficiency within a chemical manufacturing facility. Important improvements, such as improved steam systems and electric motor efficiencies or the more efficient generation of steam or power, can be accomplished at many facilities. The processes selected for Level 2 and 3 evaluations only included product specific process improvements--those changes that could be made within the process unit operations or process configuration that would result in reduced energy consumption for the production of the chemical.

The selection criteria for each energy performance level are described in more detail below.

Level 0

Level 0, the baseline case, values were determined by calculating the energy improvements included in the PEP process design and excluding these improvements from the process. Calculation of a base case served to capture the type and value of the improvements given in the PEP process and also to establish a comparable basis for comparing energy performance levels of different products.

Level 1

Level 1, the benchmarked heat integration case, was the first energy performance level to be determined for each product. A PEP process design was chosen on the basis of what process is used to manufacture the majority of the product produced in the United States, and the energy calculations were performed using the formulas in Table 5.

Level 2

Level 2 energy requirements were based on optimum heat integration of the process. This level reflects improvements in energy efficiency that can be accomplished without altering the basic process configuration. Level 2 was determined on the basis of net fuel energy consumed by the process, as the quantity and type of feedstock remains unchanged from the base case.

Pinch analysis or heat-exchange network (HEN) synthesis is used to systematically examine the heating and cooling requirements of the process. The term “pinch” refers to a key system temperature constraint that thermodynamically limits heat recovery and thermal energy efficiency. Above the pinch temperature the process system functions as a heat sink, and below the pinch temperature, as a heat source. Pinch analysis enables the matching of cold streams (streams that need heating) with hot streams (streams that need cooling) in the most effective way. In this manner, heat is exchanged internally within the process before externally supplied steam or cooling water is used.⁷

Using an algorithm adapted from examples given in Shenoy,⁸ the temperature ranges for each process stream were entered into a spreadsheet and a map of the streams is produced, which showed the process pinch temperature and the location of each hot and cold stream within the process temperature range.

Stream matches were first made between hot and cold streams above the pinch temperature, and then for hot and cold streams below the pinch temperature. Minimum approach temperatures were based on the shortcut equipment design guidelines given in Douglas.⁹ A proposed heat exchanger was considered practical if the installed cost of the heat exchange equipment (neglecting interest) could be paid for in three years or less with the energy savings resulting from the heat exchanger. A price of \$4 per million BTU of natural gas was used to calculate the savings resulting from reduced energy usage. Materials of construction for the heat exchanger were the same as those used in the PEP reports for the hot and cold streams.

After the opportunities for process stream heat exchangers were exploited, the stream data was examined for opportunities for making temperature changes within the process that would increase the opportunities for heat integration. Temperature changes that shift hot streams from below the pinch to above, or that shift cold streams from above the pinch to below, could result in further heat integration and additional savings in utilities. Temperature changes were focused on distillation columns, since distillation is a major consumer of energy in many chemical processes.

Heat pumps provide a means of upgrading heat by the input of work and are one mechanism for shifting hot streams from below the pinch to above. For this project, direct vapor recompression heat pumps were considered for distillation columns. With this type of heat pump, hot process vapors from the column overhead are compressed and then condensed in the column reboiler to satisfy the heating requirement at an elevated temperature.

Heat pumps require the input of electricity or steam to drive the compressor, as well as capital investment, so they are usually not economical unless a fairly large quantity of heat can be transferred over a fairly small temperature range. Meili¹⁰ gives the following prerequisites for the economical use of direct vapor compression employed with distillation columns:

- Reboiler duty of at least 2 MW (7 MMBtu/hr),
- Temperature rise in the compressor no more than 50 degrees C,
- No cheap waste heat available for heating the column, and
- Column head pressure exceeds 10,000 Pa (1.5 psia),

These guidelines were used to check the process stream spreadsheet map for a stream combination (a hot stream below the pinch and a cold stream above the pinch) that might meet these guidelines. The hot and cold streams could be located on the same distillation column or on two different columns in the separation train. If the prerequisites given above were met, the heat pump configuration was simulated, and the cost of the new system was estimated. A payback period of three years or less was used as the criterion to determine whether or not the heat pump system was practical.

Another way to shift streams through the pinch is to change the operating temperature of a distillation column or to add side reboilers or condensers. For this project, temperature changes were limited to a range of 10° C. Temperature and pressure changes were

approached with caution, since such changes can create effects, such as product decomposition, which are beyond the scope of this project to predict. The three-year payback period was again the economic criteria for determining whether process changes were practical. For the five products studied in this project, temperature adjustments within this limited range did not present any additional opportunities for heat integration.

The combination of options chosen to represent Level 2 consists of those options that met the economic criteria and together yielded the lowest net fuel energy consumed.

Level 3

Level 3, process redesign, energy requirements were based on an alternate process configuration that was estimated to yield a further level of improvement in energy efficiency. The reaction chemistry for Level 3 remained the same as for the base case.

For Level 3, the following types of modifications to the base case were considered:

- Material selection,
- Unit operation design,
- Process integration and recycle structure, and
- Utility design and fluid handling.

The analysis of each flowsheet began with material selection. Although the primary raw materials used in the process were fixed, alternative catalysts, solvents (used as reaction media or separating agents), and oxidizing agents (e.g., pure oxygen versus air) were considered. The primary sources of data on alternative materials were PEP reports and the patent literature.

After considering alternative materials, alternative unit operations were investigated. These included alternative reactor configurations (e.g., staged reactors rather than a single reactor), and alternative separation mechanisms (e.g., use of solvent extraction rather than distillation). Again, the primary sources of data on alternative materials were PEP reports and the patent literature.

Process integration and recycle structure in Level 3 focused on different issues than in Level 2. Level 2 analyses examined the use of heat exchange networks for improving the process performance, while Level 3 examined the use of material recycle and integration. For example, in reversible partial oxidation reactions, the recycle of by-products to the reactor can inhibit the formation of additional undesired by-products¹¹, improving selectivity to the desired products.

Finally, fluid handling was an important consideration. Compression is a significant energy sink in many chemical processes and reductions in pressures used in the process or reducing the throughput handled by compressors can influence process energy requirements. Recycle opportunities and mechanisms for reducing process pressures were considered.

Allen and Shonnard¹¹ provide detailed descriptions of the types of alternatives that can be considered when evaluating material selection, unit operation design, process recycle structure and fluid handling. In general, these methods generate a wide range of complementary and conflicting process changes. For example, replacing a homogeneous catalyst with a supported catalyst that improves selectivity both reduces by-products generated in the reactor and reduces the complexity of the separation train by eliminating the need to recover a homogeneous catalyst. In this case, process changes are complementary. In contrast, recycling undesired by-products produced in a reversible reaction to the reactor to improve selectivity can increase the complexity and energy consumption of the separation network. This is a modification that introduces conflicting process changes. Further complicating the evaluation of Level 3 alternatives, the feasibility of many of the process changes was unclear, even though the majority of the process alternatives were drawn from PEP reports and the patent literature. Thus, the selection of a Level 3 process configuration was complex.

The selection of a Level 3 process configuration and the energy calculations for Level 3 were based on:

- Process design information from PEP reports and reviews,
- Engineering estimates of the potential energy savings that could result from a process change, and
- Results of computer process simulations for proposed process changes.

The selection of the Level 3 process configuration took into consideration the total energy (fuel plus raw material energy) consumed in the process and product chain net as well as net fuel energy consumed in the process. For two processes that use the same feedstock, but in differing quantities, the raw material energy consumed per pound of product becomes an important factor and the total energy consumed in the process is used as the criterion for selecting the Level 3 configuration. When a different feedstock was used, such as oxygen instead of air, the total energy consumed in the product chain became the energy criterion for the decision.

Level 3 also took into consideration the economic feasibility of the new process configuration. Economic estimates from PEP reports and the literature were used to judge the practicality of the redesigned process compared to the base case. When PEP process designs were available for Level 3 options the SRI product value, which is defined as the net production cost plus 25% per year pretax return on fixed capital, was used as the economic criterion. If the product value of the Level 3 design was equal to or lower than that for the base process, the criterion for economic practicality was satisfied.

Level 4

Energy requirements were calculated in terms of standard enthalpies for consistency and simplicity. The change in enthalpy for a reaction represents the total energy exchange that takes place between the chemical reaction system and its environment. This change in enthalpy at standard conditions, or the standard heat of reaction, is used to represent the theoretical energy requirement for the process. The standard heat of reaction is calculated as

$$\Delta H^{\circ} = \Sigma(\Delta H^f)_{\text{products}} - \Sigma(\Delta H^f)_{\text{reactants}}$$

where ΔH^f equals the enthalpy of formation at 289° K and 1 atm. When ΔH° is negative, energy is released from the chemical reaction. When ΔH° is positive, energy must be added to the reaction.

The Gibbs free energy change for the reaction is also calculated for the ideal reactions and these values are presented in Table 7, along with the standard heats of reaction. The standard free energy is calculated as:

$$\Delta G^{\circ} = \Sigma(\Delta G^f)_{\text{products}} - \Sigma(\Delta G^f)_{\text{reactants}}$$

where ΔG^f equals the free energy of formation at 289° K and 1 atm.

The Gibbs free energy is a measure of the energy which is available to do work. It is related to the heat of reaction by the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

where T equals the temperature of the reaction and ΔS° is the standard entropy change for the reaction. The value of ΔG° is positive when energy is consumed in the reaction, and negative when energy is generated.

Table 7. Standard Heat of Reaction and Gibbs Free Energy of Reaction for the Ideal Equations

Product	Ideal Reaction	ΔH° (BTU/lb)	ΔG° (BTU/lb)
Acetic Acid	$\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}$	-868	-534
Acetic Anhydride	$1.5\text{CH}_3\text{OH} + \text{CH}_3\text{COOH} + 1.5\text{CO} \rightarrow$ $(\text{CH}_3\text{CO})_2\text{O} + 0.5\text{CH}_3\text{COOH} + \text{H}_2\text{O}$	-558	-290
Maleic Anhydride	$\text{C}_4\text{H}_{10} + 3.5 \text{O}_2 \rightarrow \text{C}_4\text{H}_2\text{O}_3 + 4 \text{H}_2\text{O}$	-5,524	-5,582
Terephthalic Acid	$\text{C}_8\text{H}_{10} + 3 \text{O}_2 \rightarrow \text{C}_8\text{H}_6\text{O}_4 + 2 \text{H}_2\text{O}$	-3,160	-3,051
Caprolactam	$\text{C}_6\text{H}_{12} + \text{O}_2 + \text{NH}_3 \rightarrow \text{C}_6\text{H}_{11}\text{NO} + 2$ H_2O	-2,133	-2,068

The heat and free energy of reactions were calculated from data reported in Daubert and Danner.¹²

3. ENERGY PERFORMANCE RESULTS

3.1 Acetic Acid

Acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, CAS# 64-19-7), is used in the production of acetic anhydride, vinyl acetate and a variety of acetate esters. Vinyl acetate is used in the manufacture of paints, adhesives and paper coatings. Acetic anhydride is used in making cellulose acetate filters and cellulosic plastics. Worldwide annual production of acetic acid is approximately 4 million tons.

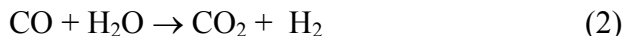
Acetic acid is primarily produced via the low-pressure carbonylation of methanol, although prior to the invention of this process by Monsanto¹³, acetic acid was also manufactured via the partial oxidation of acetaldehyde, butane, or butylene. Since 1973, over 90 percent of all new acetic acid capacity has been based on Monsanto's process, and in 1992, the Monsanto process accounted for greater than 50 percent of the world's acetic acid capacity.¹⁴

The Base Process

Production of acetic acid via the carbonylation of methanol will be used as the base case in this analysis. Typically, methanol carbonylation is conducted using a homogeneous rhodium catalyst in conjunction with an iodide promoter (see, for example, Forster and Dekleva, 1986¹⁵). The reaction is conducted at approximately 180-200°C, with a 10^{-3} M rhodium concentration at 30-40 atmospheres of pressure. The desired reaction is:



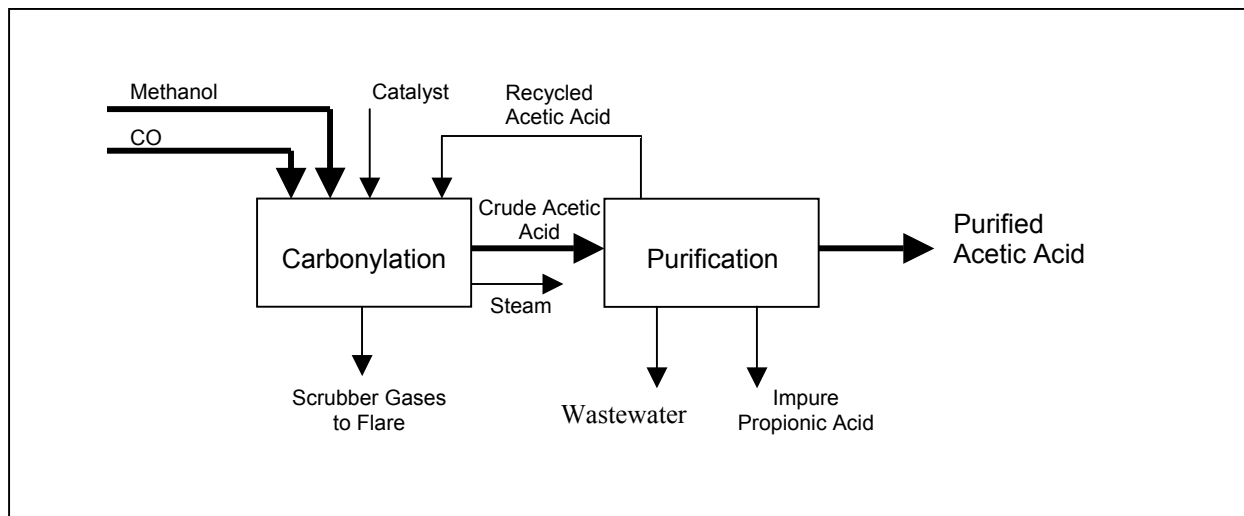
The undesired reactions include:



The carbonylation reaction is typically done in the presence of significant quantities of water, since the rhodium catalyst can tend to precipitate in the presence of less than 10-20% by weight water. Selectivity (based on methanol) is very high, typically 99% or more. The major inefficiency in the reaction is loss of carbon monoxide to hydrogen and CO_2 , via the water gas shift reaction (approximately 90% selectivity to acetic acid based on CO). Heavy ends, particularly formic acid and propionic acid, are also produced. The effluent from the reactor is fed to a separation train, where a series of distillation columns are used to recover the catalyst and promoter, as well as to separate the acetic acid from water and heavy ends. The base process is based on PEP Report 37B¹⁴.

Figure 4. Base Process for Acetic Acid Production

From methanol via low-pressure carbonylation with homogeneous rhodium catalyst.



As shown in Figure 4, the base process consists of two major sections, which are described below.

Carbonylation Section: Carbon monoxide, methanol and catalyst are fed to the carbonylation reactor. A reactor cooler is used to remove the heat of reaction and generate 150-psig steam, at quantities in excess of the process requirements. (The major steam requirements are for higher pressure steam.) Unreacted gases from the reactor are passed through a vent gas scrubber. A stripper is used to strip a recycled acetic acid stream from the downstream refining column before returning it to the carbonylation reactor.

Purification Section: Product from the carbonylation reactor is purified in a series of four distillation columns: a crude fractionating column, a dehydration column, an excess water column, and a refining column. Acetic acid product is taken as a side stream from the refining column. The bottom stream from the refining column receives further treatment in the heavy ends stripper, where impure propionic acid is recovered as a by-product.

Energy Performance Levels

A summary of the energy performance levels for acetic acid is given in Table 8. Subsequent sections describe the determination of each level.

Table 8. Energy Performance Levels for the Production of Acetic Acid

Energy requirements in BTU per pound of product.

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	Level 1	Level 2	Level 3	Level 4
Electricity Requirement	103	103	103	148	
Hot Utility Requirement	1,555	1,555	1,529	1,391	
Hot Utility Credit	-363	-363	-363	-401	
Net Power & Hot Utility Requirements	1,295	1,295	1,269	1,138	
Fuel Energy for Electricity Generation	333	333	333	476	
Fuel Energy for Steam/Heat Transfer Fluid	2,692	2,692	2,650	2,275	
<u>Total Fuel Energy Required</u>	3,024	3,024	2,982	2,751	
Fuel Energy Credit	-572	-572	-572	-632	
Net Fuel Energy Consumed	2,452	2,452	2,411	2,120	-867
Raw Material Energy Consumed in Process	1,173	1,173	1,173	1,173	867
Total Energy Consumed in Process	3,625	3,625	3,584	3,293	0
Total Energy Consumed in Feedstock Production	18,802	18,802	18,802	18,802	0
Total Energy Consumed in Product Chain	22,427	22,427	22,386	22,095	0

Level 0—Base Process: From methanol via low-pressure carbonylation with homogeneous rhodium catalyst.

Level 1—Benchmarked Heat Integration: No improvements are added to the base process.

Level 2—Optimum Heat Integration: One process stream heat exchanger is added to the base process.

Level 3—Process Redesign: From methanol via low-pressure carbonylation with heterogeneous rhodium catalyst.

Level 4—Theoretical Energy Requirement with 100% conversion of methanol and carbon monoxide and 100% selectivity to acetic acid. The Gibbs free energy for the ideal reaction is -534 BTU/lb acetic acid.

Level 0: Energy Requirements for the Base Process

Table 9 below summarizes the energy requirements for the base case. The air compressor for the air feed to the reactors takes approximately 11 percent of the total fuel energy for the process. The major heat requirement occurs in the purification section, where the heat required for the crude fractionating column reboiler takes approximately 57 percent of the total fuel energy for the process. Fuel energy is credited for the steam generated in the reactor cooler.

Table 9. Level 0 Energy Requirements for Acetic Acid Production

Base Case: From methanol via low-pressure carbonylation with homogeneous rhodium catalyst. Energy requirements in BTU per pound of product.

	Carbonylation Section	Purification Section	Total Process
Electricity Requirement	101	2	103
Hot Utility Requirement	137	1,418	1,555
Hot Utility Credit	-363	0	-363
Net Power & Hot Utility Req.	-125	1,420	1,295
Fuel Energy for Electricity Generation	327	6	333
Fuel Energy for Steam/Heat Transfer Fluid	215	2,477	2,692
<i>Total Fuel Energy Required</i>	542	2,482	3,024
Fuel Energy Credit	-572	0	-572
Net Fuel Energy Consumed	-30	2,482	2,452

Level 1: Energy Requirements for the Benchmarked Heat Integration Case

The energy requirements for the PEP Benchmark case and the base process are identical.

Level 2: Energy Requirements for Optimum Heat Integration

Process Stream Heat Exchangers

In the base process, the heat of reaction is used to heat boiler feed water. The 150 psig steam generated is adequate to meet several of the heat requirements in the process. Since the reaction is carried out at less than 200°C, and because the flash effluent is fed to a separation column at nearly reactor temperature, there are few opportunities for significant additional heat integration. It is possible to drive the reboiler of the reactor gas stripper with the product cooler from the refining column or the dehydration column condenser. Approximately 42 BTU of fuel energy per pound of product could be saved by using a process stream heat exchanger instead of steam to provide the heat required for this reboiler, and the cost of the exchanger could be recovered within three years.

Heat Pumps

Although process stream matches exist which meet the prerequisites for the application of heat pumps, the required material of construction is zirconium, and the expense of the additional equipment makes heat pump systems impractical, according to the economic criterion.

Level 2 energy requirements are summarized in Table 10. Compared to the Level 0 base process, they constitute about 1-2% savings in the net fuel energy consumed.

Table 10. Level 2 Energy Requirements for Acetic Acid Production

Optimum Heat Integration: From methanol via low-pressure carbonylation with homogeneous rhodium catalyst and one process stream heat exchanger. Energy requirements in BTU per pound of product.

	Carbonylation Section	Purification Section	Total Process
Electricity Requirement	101	2	103
Hot Utility Requirement	110	1,418	1,529
Hot Utility Credit	-363	0	-363
Net Power & Hot Utility Req.	-152	1,420	1,269
Fuel Energy for Electricity Generation	327	6	333
Fuel Energy for Steam/Heat Transfer Fluid	173	2,477	2,650
<i>Total Fuel Energy Required</i>	500	2,482	2,982
Fuel Energy Credit	-572	0	-572
Net Fuel Energy Consumed	-72	2,482	2,411

Level 3: Energy Requirements for Process Redesign

Selected Option for Level 3

The process redesign option chosen for Level 3 is in the category of *Material Selection*. The main material choices, beyond the feed materials (methanol and CO) which were considered to be fixed, are the catalyst and the promoter. Choice of catalyst/promoter systems can affect energy efficiency by influencing the energy requirements of the downstream separations.

In the acetic acid process, the base process catalyst/promoter system consists of a rhodium based homogeneous catalyst and an iodide promoter. With this catalyst/promoter system, the carbonylation reaction is typically done in the presence of significant quantities of water, since the rhodium catalyst can tend to precipitate in the presence of less than 10-20% by weight water. This addition of water necessitates significant energy and capital investments in downstream separations. The use of a homogeneous, rather than a heterogeneous system, also necessitates the use of downstream separations, in this case, to recover catalyst and promoter.

Two process modifications in the area of material selection were considered to improve the energy efficiency of the process—use of a heterogeneous rhodium catalyst and use of a catalyst system that does not require water. The redesign option which yielded the greatest energy savings based on the information available was a design for a low pressure methanol carbonylation process with a heterogeneous-supported rhodium catalyst and methyl iodide promoter. The design is based on PEP Review 97-12¹⁶ and the process is intended to resemble the Chiyoda/UOP *Acetica*TM process, (US 5,334,755) in

which the active rhodium complex is chemically immobilized on a polyvinylpyridine resin. The major sections of the process are the same as shown in Figure 4.

The energy requirements for the process are given in Table 11. Compared to the Level 0 base process, they constitute 9% savings in the total fuel energy required and 10% increase in fuel energy generated. Together, the improvements make up 14% savings in the net fuel energy consumed, which is 13 percentage points more than Level 2. Energy savings occur in this process because less energy is required to accomplish the purification of the product. (The quantity of feedstock consumed per pound of acetic acid product and the type of feedstock are not changed in this case, so the net fuel energy consumed by the process is the appropriate energy criterion for selecting the Level 3 option.)

According to PEP Review 97-12, the estimated capital investment for the *Acetica*TM process is lower than that for the base process. For a plant production capacity of 800 million pounds per year, capital investment for the *Acetica*TM process is estimated to be approximately \$150 million, compared to \$165 million for the homogeneous catalyst process. The product value for the Acetica process is estimated to be \$0.1520, compared with \$0.1630 for the base process.

Table 11. Level 3 Energy Requirements for Acetic Acid Production

Process Redesign: From methanol via low-pressure carbonylation with heterogeneous rhodium catalyst. Energy requirements in BTU per pound of product.

	Carbonylation Section	Purification Section	Total Process
Electricity Requirement	144	4	148
Hot Utility Requirement	110	1,281	1,391
Hot Utility Credit	-401	0	-401
Net Power & Hot Utility Req.	-147	1,285	1,138
Fuel Energy for Electricity Generation	463	13	476
Fuel Energy for Steam/Heat Transfer Fluid	173	2,102	2,275
Total Fuel Energy Required	636	2,115	2,751
Fuel Energy Credit	-632	0	-632
Net Fuel Energy Consumed	5	2,115	2,120

Additional Options Considered for Level 3

Material Selection

The alternative option evaluated in the area of material selection was the use of a catalyst system that does not require water, which has been associated with large potential energy savings. Two 1997 patents from BP Chemicals Limited (U.S. Patents 5,877,348 and 6,140,535) report the use of an iridium carbonylation catalyst with methyl iodide promoter, in which the reactor operates at less than 8% water. BP Amoco's iridium-based Cativa technology is installed in Sterling's Texas City acetic acid plant, and is reported to

give an acetic acid yield of 98% and operating savings of 10 to 30 percent compared with rhodium-based systems. (PEP Review 97-12)

Our process simulation indicated that the lower water content reduces the separation requirements from 5 distillation columns in our Level 1 PEP Base Case to 2 distillation columns — a reduction in capital cost that is consistent with the BP Chemicals patents. However, according to our process simulation, the energy utilization in the two columns was of the same magnitude as that required in the base case separation train. Considering the error margin in the energy estimates from our process simulation, the total energy use for the iridium process is virtually identical to that in the PEP base process.

Unit operation design

If the homogeneous rhodium catalyst continues to be used, then a variety of improvements to the separation train could be considered to improve energy efficiency. Most of these improvements involve alternatives to distillation for recovering catalyst and purifying products. For example, U.S. Patent 5,662,780 (March, 1996) describes the use of isopropyl acetate as an extracting solvent, with recovery of acetic acid and regenerated extracting solvent in an azeotropic distillation, however sufficient information was not available to make an accurate comparison of the energy requirements and economic feasibility of this option compared to the base process.

Other improvements (U.S. Patents 5,620,567, 5,756,836) describe the use of reactive agents to remove trace impurities in the product acetic acid. The treatments include acid washing (e.g., phosphoric acid or toluene sulfonic acid) and ozone treatment. These processes may find use in the production of fine chemical grade acetic acid.

Process integration and recycle structure

Among the streams generated in the base case process are aqueous streams containing up to 20% acetic acid (e.g., the dilute acid light phase from the splitter column or the aqueous bottom phase from the distillation to recover methyl iodide). U.S. Patent 5,599,976 (February, 1997) describes reacting these dilute aqueous acetic acid streams with methanol over an acid catalyst, to form methyl acetate and water modifications. The methyl acetate and water are separated and the methyl acetate is recycled to the carbonylation reactor.

This improvement could not be adequately evaluated with the information available.

Utility design and fluid handling

Feed compression is the main energy sink in the fluid handling system, however, it is unlikely that the pressure requirements could be reduced unless the catalyst is modified.

Level 4: Theoretical Energy Requirements

The heat of reaction for the ideal reaction at standard conditions is -867 BTU/lb of acetic acid. The change in the Gibbs free energy of the ideal reaction at standard conditions is -534 BTU/lb of acetic acid.

3.2 Acetic Anhydride

Acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$, CAS# 108-24-7), is used primarily in the production of cellulose acetate, and approximately 1 million tons are produced annually in the United States. The largest single end-use of cellulose acetate is in the manufacture of cigarette filters. A secondary, but declining application is textile fibers.

Acetic anhydride is produced via the thermal decomposition of acetic acid (ketene process), the direct oxidation of acetaldehyde, and the carbonylation of methyl acetate. The main process for acetic anhydride manufacture in the U.S. is based on the carbonylation of methyl acetate.

The Base Process

The base process is the design offered in PEP Report 37B¹⁴, which is for an integrated methyl acetate/acetic anhydride plant designed to represent the Eastman process. The methyl acetate production section is based on patent US 4,435,595 (Eastman Kodak) and a 1990 article in *Chemical Engineering Progress*¹⁷. The base process is designed for the co-production of acetic anhydride and acetic acid. Energy requirements are calculated for a product ratio of 0.3 pounds of acetic acid produced per pound of acetic anhydride, and are expressed as BTU per pound of acetic anhydride.

Three main reactions occur in the process. The first is the reaction between acetic acid and methanol to form methyl acetate. In the Eastman process by-product acetic acid from cellulose esters manufacture is used as the feed to produce methyl acetate. Two reactions occur in the carbonylation reactor. One is the reaction of methyl acetate and carbon monoxide to form acetic anhydride and the other is the reaction between acetic anhydride and methanol to form acetic acid and methyl acetate. The overall reaction for the process can be expressed as:



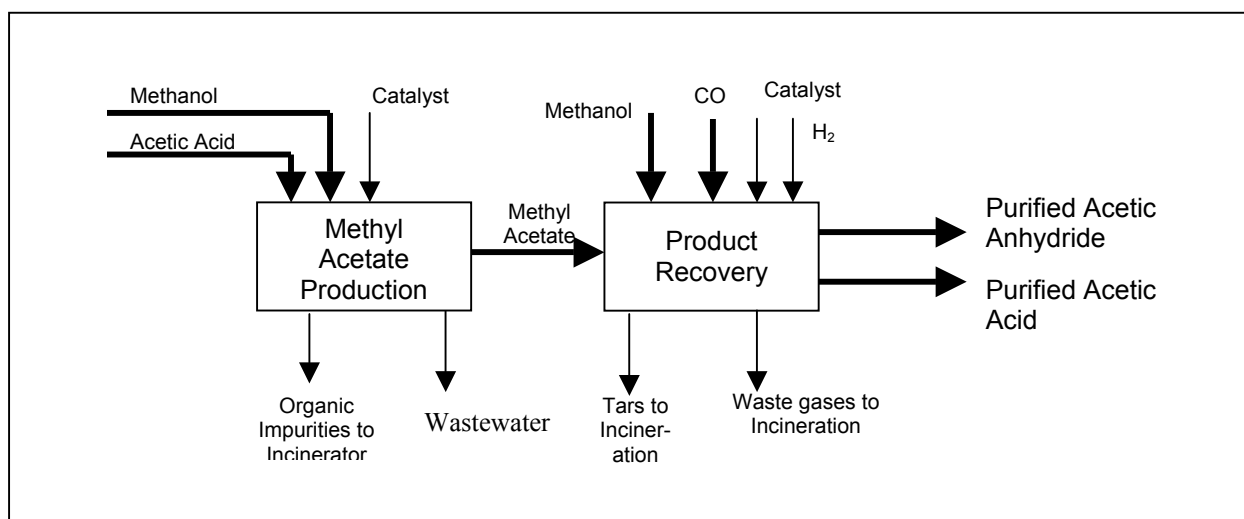
The major undesired reaction is the formation of tars.

As shown in Figure 5, the base process is consists of two major sections, which are described below.

Methyl Acetate Production Section: In the base process, acetic acid, methanol and sulfuric acid catalyst are fed to a reactor-distillation column. The high-purity methyl acetate product is routed to the Product Recovery Section.

A side stream from the reactor is routed through a series of two distillation columns to remove organic impurities. The bottom stream from the reactor is treated in one distillation column to recover methanol, which is recycled to the reactor.

Figure 5. Base Process for Acetic Anhydride Production
From methanol and acetic acid via methyl acetate carbonylation.



Product Recovery Section: The methyl acetate stream, carbon monoxide, hydrogen, methanol and catalyst are fed to the carbonylation reactor. A homogeneous rhodium catalyst in conjunction with methyl iodide and lithium iodide promoters is used. Hydrogen is added to the reactor primarily to suppress the formation of tar, but has also been found to increase the reaction rate.¹⁸ Methanol is added for the production of acetic acid. The heat of reaction is removed by circulation of the reaction product through a reactor cooler, where steam is generated.

The reaction product is routed to an evaporator flash vessel and a wiped film evaporator before being treated in a series of columns: the light ends column, the low boilers column, the acetic acid column, where acetic acid is the overhead product, and the acetic anhydride column, where acetic anhydride product is drawn from the side of the column.

Overhead vapors from the carbonylation reactor are compressed and recycled to the reactor. Waste gases are scrubbed prior to incineration. (The energy required for incineration is not included in the energy requirements for this process.)

Catalyst is recovered from the purge stream from the wiped-film evaporator. A second wiped-film evaporator, and an extraction column, and a methyl iodide recovery column are used to recover methyl iodide. Tars from the methyl iodide column are incinerated.

Energy Performance Levels

A summary of the energy performance levels for acetic anhydride is given in Table 12. Subsequent sections describe the determination of each level.

Table 12. Energy Performance Levels for the Production of Acetic Anhydride
Energy requirements in BTU per pound of acetic anhydride product. *(Important, because co-product is produced, but calculations are based on pounds of acetic anhydride only.)*

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	Level 1	Level 2	Level 3	Level 4
Electricity Requirement	97	97	150	152	
Hot Utility Requirement	1,294	1,284	955	925	
Hot Utility Credit	-316	-316	-316	-304	
Net Power & Hot Utility Requirements	1,075	1,065	789	773	
Fuel Energy for Electricity Generation	312	312	482	489	
Fuel Energy for Steam/Heat Transfer Fluid	1,945	1,929	1,439	1,394	
<u>Total Fuel Energy Required</u>	<u>2,256</u>	<u>2,241</u>	<u>1,921</u>	<u>1,883</u>	
Fuel Energy Credit	-468	-468	-468	-450	
Net Fuel Energy Consumed	1,788	1,773	1,453	1,432	-558
Raw Material Energy Consumed in Process	997	997	997	785	558
Total Energy Consumed in Process	2,785	2,770	2,450	2,217	0
Total Energy Consumed in Feedstock Production	23,207	23,207	23,207	22,314	0
Total Energy Consumed in Product Chain	25,992	25,977	25,657	24,531	0

Level 0: Base Process—from methanol and acetic acid via methyl acetate carbonylation.

Level 1: Benchmarked Heat Integration—Base process is improved with one process heat exchanger.

Level 2: Optimum Heat Integration—Base process is further improved with the addition of a heat pump.

Level 3: Process Redesign-- from methanol and acetic acid via methyl acetate carbonylation plus process stream heat exchanger and heat pump and secondary carbonylation reactor assuming a 4% increase in production.

Level 4: Theoretical energy requirement with 100 percent conversion of methanol. The Gibbs free energy for the ideal reaction = -290 BTU/lb

Level 0: Energy Requirements for the Base Case

Table 13 below summarizes the energy requirements for the base case. The major heat requirement occurs in the product recovery section, where the heat required for the acetic acid column takes approximately 27 percent of the total fuel energy required for the process. Fuel energy is credited for the steam generated in the carbonylation reactor cooler.

Table 13. Level 0 Energy Requirements for Acetic Anhydride Production

Base Case: From methanol and acetic acid via methyl acetate carbonylation

Energy requirements in BTU per pound of acetic anhydride product.

	Methyl Acetate Production Section	Product Recovery Section	Total Process
Electricity Requirement	2	94	97
Hot Utility Requirement	482	813	1,294
Hot Utility Credit	0	-316	-316
Net Power & Hot Utility Requirements	484	591	1,075
Fuel Energy for Electricity Generation	8	304	312
Fuel Energy for Steam/Heat Transfer Fluid	713	1,231	1,945
<u>Total Fuel Energy Required</u>	721	1,535	2,256
Fuel Energy Credit	0	-468	-468
Net Fuel Energy Consumed	721	1,067	1,788

Level 1: Energy Requirements for the Benchmarked Heat Integration Case

The PEP benchmark case includes one process stream heat exchanger, which results in a small energy savings of about 15 BTUs per pound of acetic anhydride. The hot wastewater stream from the methanol recovery column is used to heat the methanol feed to the methyl acetate reactor.

Level 1 energy requirements are summarized in Table 14. The energy savings from the Level 0 base case is less than 1%.

Table 14. Level 1 Energy Requirements for Acetic Anhydride Production

Benchmarked Heat Integration: From methanol and acetic acid via methyl acetate carbonylation with one process stream heat exchanger.

Energy requirements in BTU per pound of acetic anhydride product.

	Methyl Acetate Production Section	Product Recovery Section	Total Process
Electricity Requirement	2	94	97
Hot Utility Requirement	471	813	1,284
Hot Utility Credit	0	-316	-361
Net Power & Hot Utility Requirements	474	591	1,065
Fuel Energy for Electricity Generation	8	304	312
Fuel Energy for Steam/Heat Transfer Fluid	698	1,231	1,929
<u>Total Fuel Energy Required</u>	705	1,535	2,241
Fuel Energy Credit	0	-468	-468
Net Fuel Energy Consumed	705	1,067	1,773

Level 2: Energy Requirements for Optimum Heat Integration***Process Stream Heat Exchangers***

The carbonylation of methyl acetate to form acetic anhydride is an exothermic reaction and in the base process, the heat of reaction is used to heat boiler feed water. The steam

that is generated is adequate to meet the heat requirements of several of the unit operations. The remaining significant heat sources in this process are not at temperatures high enough to enable heat exchange with the cold streams, so no additional process stream heat exchangers are recommended.

Heat Pumps

An opportunity for a heat pump is present in the product recovery section. The reboiler of the acetic acid column can be driven by the overhead condenser of the acetic anhydride column, resulting in fuel energy savings of 317 BTUs per pound of acetic anhydride.

Level 2 energy requirements are summarized in Table 15. Compared to the Level 0 base process, they constitute 15% savings in total fuel energy required, and 19% savings in net fuel energy consumed.

Table 15. Level 2 Energy Requirements for Acetic Anhydride Production

Optimum Heat Integration: From methanol and acetic acid via methyl acetate carbonylation with one process stream exchanger and heat pump.

Energy requirements in BTU per pound of acetic anhydride product.

	Methyl Acetate Production Section	Product Recovery Section	Total Process
Electricity Requirement	2	147	150
Hot Utility Requirement	471	483	955
Hot Utility Credit	0	-316	-316
Net Power & Hot Utility Requirements	474	315	789
Fuel Energy for Electricity Generation	8	475	482
Fuel Energy for Steam/Heat Transfer Fluid	698	741	1,439
<u>Total Fuel Energy Required</u>	705	1,216	1,921
Fuel Energy Credit	0	-468	-468
Net Fuel Energy Consumed	705	747	1,453

Level 3: Energy Requirements for Process Redesign

Selected Option for Level 3

The process redesign option chosen for Level 3 is in the category of *Unit Operation Design*. The base case process for acetic anhydride involves a single carbonylation reactor; however, recent patents indicate that the energy efficiency of acetic anhydride production via the carbonylation of methyl acetate can be improved by introducing a secondary carbonylation reactor, which utilizes unreacted CO.

U.S. Patent 5,922,911 July, 1999 reports an improved efficiency associated with a two-stage reactor. The first stage in the two-stage reactor is operated in the same manner as the base case carbonylation reactor – CO is sparged into the reaction mix. As described in the patent, the liquid effluent from the first reactor is sprayed into a second reactor,

which is maintained at 30-50 bar (vapor phase is largely CO, with up to 7% hydrogen). The temperature is not specified, but the patent implies that no cooling or heating occurs between the first and second reactors. The reactor is operated as a two-phase system, with CO fed to the vapor phase, rather than being sparged into the liquid, as in the first reactor. The residence time in the second reactor is approximately 4-10 minutes, compared to 2.4 hours in the first reactor. The base process assumes a 62% per pass conversion of methyl acetate. With the secondary reactor, a 4-5% increase in the per-pass conversion is expected based on the patent information.

In our calculation, we assumed that this could lead to an overall 4% increase in yield. The increase in yield reduces the per-pound energy requirements in the unit operations upstream of the carbonylation reactors. However, the per-pound energy requirement for product separation downstream of the reactor was assumed to be identical to the base case. In reality, because of the improved purity associated with the greater yield, the energy required for separation is likely to be lower. Therefore, the energy savings resulting from the addition of the secondary reactor should be viewed as a conservative estimate.

As shown in Table 16, the secondary carbonylation reactor results in 17% savings in total fuel energy required from the Level 0 base case. However, it also resulted in 4% decrease in fuel energy generated. Together, these changes resulted in approximately 20% savings in net fuel energy consumed from Level 0.

Economic information was not available specifically for this modification, however, estimates were made using the PEP cost data for the single carbonylation reactor and a cost calculation similar to that for Level 2 improvements. Using a value of 356 BTU of fuel energy saved per pound of product (from Level 0), and a fuel cost of \$4 per MMBTU, the payback period was calculated to be 3.9 years. Considering the estimated energy savings are conservative, the modification was judged to be economically practical.

Table 16. Level 3 Energy Requirements for Acetic Anhydride Production

Process Redesign: From methanol and acetic acid via methyl acetate carbonylation plus process stream heat exchanger, heat pump and secondary carbonylation reactor assuming a 4% increase in yield. Energy requirements in BTU per pound of acetic anhydride product.

	Methyl Acetate Production Section	Product Recovery Section	Total Process
Electricity Requirement	2	149	152
Hot Utility Requirement	453	472	925
Hot Utility Credit	0	-304	-304
Net Power & Hot Utility Requirements	456	317	773
Fuel Energy for Electricity Generation	7	482	489
Fuel Energy for Steam/Heat Transfer Fluid	671	723	1,394
<u>Total Fuel Energy Required</u>	678	1,204	1,883
Fuel Energy Credit	0	-450	-450
Net Fuel Energy Consumed	678	754	1,432

Additional Options Considered for Level 3

Unit operation design

Alternative options considered in the area of unit operation design involved separation operations. A number of recent patents describe improvements to the catalyst recovery operations (U.S. Patents 5,380,929 5,554,790, 5,648,531). The Kirk-Othmer Encyclopedia (1992)¹⁹ also suggests alternative methods for catalyst recovery. Relatively few data are provided in these patents, however, so detailed designs of improved catalyst recovery operations were beyond the scope of this project. Nevertheless, the energy consumption associated with the catalyst recovery units should be considered variable and assuming 10-20% efficiency improvements may be an appropriate first approximation.

Material selection

The main material choices, beyond the feed materials (methyl acetate and CO) that will be considered fixed, were the catalyst and the promoter. Choice of catalyst/promoter systems can affect energy efficiency by influencing the energy requirements of the downstream separations. In particular, if a less expensive alternative to the rhodium catalyst can be identified, then the efficiency and the energy intensity of the catalyst recovery processes can be lowered, and the separation of the catalyst from the tars generated in the reactor is not as critical.

A variety of references have identified nickel catalysts (U.S. Patents 4,440,570, 4,442,304, 4,557,760, 4,578,368, and 4,650,649, as well as Gong, et al., 1999²⁰), and although kinetic data sufficient for process design calculations are available in the literature, nickel catalysts do not yet appear to be used in commercial applications. It may also be possible to use a heterogeneous rhodium catalyst. There are reports of supported rhodium catalysts (e.g., European Patent 180,802 October, 1986). However, the literature is unclear on whether catalyst lifetimes in a fixed bed application are sufficiently long.

Because of the lack of literature on the commercial application of these alternative catalytic materials, the energy efficiency improvements associated with these alternative materials were not evaluated.

Process integration and recycle structure

Among the streams generated in the base case process is waste carbon monoxide, which is incinerated. In the redesign option selected for Level 3, this waste CO stream is recycled to a secondary reactor that results in increased conversions (based on methyl acetate).

Utility design and fluid handling

Feed compression is the main energy sink in the fluid handling system, however, it is unlikely that the pressure requirements could be reduced unless the catalyst is modified.

Level 4: Theoretical Energy Requirements

The heat of reaction for the ideal reaction at standard conditions is –558 BTU per pound of acetic anhydride. The change in the Gibbs free energy of the ideal reaction at standard conditions is –290 BTU per pound of acetic anhydride.

3.3 Maleic Anhydride

Maleic anhydride ($C_4H_2O_3$, CAS# 108-31-6), or 2,5 furandione, is used in the production of polyester resins. These resins are used in a variety of applications, ranging from automobile bodies to bathroom fixtures. Maleic anhydride is also used in the production of pesticides, plasticizers and lubricants.

Prior to 1974, most maleic anhydride was produced via the partial oxidation of benzene. Benzene, although easily oxidized to maleic anhydride with high selectivity, is an inherently inefficient feedstock, since two excess carbon atoms are present in the raw material. Rapid increases in the price of benzene and the recognition of benzene as a hazardous material intensified the search of alternative process technology in the U.S.²¹ In 1974, Monsanto began producing maleic anhydride from n-butane. Since that time, virtually all manufacturing operations in the United States have converted to the use of n-butane as a feedstock, although facilities in some locations, where n-butane is relatively unavailable, continue to use the benzene process.

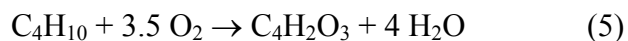
There are two main production routes for maleic anhydride from n-butane; fixed bed production, which was employed in the original butane to maleic anhydride process, and newer fluid-bed designs. Fluid bed technology was introduced in 1989 to plants in the Far East, but the U.S. remains committed to fixed bed technology.²²

There are also two major methods of product recovery. Maleic anhydride is recovered from the reactor effluent either by organic solvent scrubbing or by water scrubbing. Organic solvent-based systems are more energy efficient and have a higher recovery of maleic anhydride. Energy needs of the closed-loop solvent recovery system can be roughly one third that of an aqueous system, and approximately 97-98 percent of the maleic anhydride produced in the reactor can be recovered with an organic system, compared to recovery rates of 92-95 percent, which are typical for a water-based system.²³

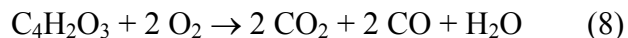
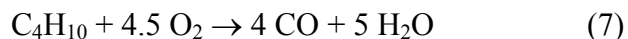
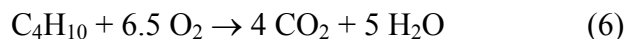
The Base Process

The base case for the determination of minimum energy levels is the fixed-bed process for maleic anhydride production from n-butane. The process is based on PEP Review 93-2-3²², which matches the processes described in US patents 6,005,121 (Monsanto), 6,040,460 (Pantochim), and 6,120,654 (Huntsman). An organic solvent system is used for product recovery (PEP Review 93-2-3 and U.S. patent 4,314,946 (Ftalital)). The solvent used in the base case is dibutyl phthalate, which according to PEP Review 93-2-3, is the solvent likely to be used in practice.

The major sections of the base process are shown in Figure 6. In the reaction section a mixture of compressed air and n-butane is fed to fixed bed reactors where the butane is oxidized to maleic anhydride over a phosphorus-vanadium-oxide catalyst. The desired reaction is:



Several undesired reactions can occur, however:

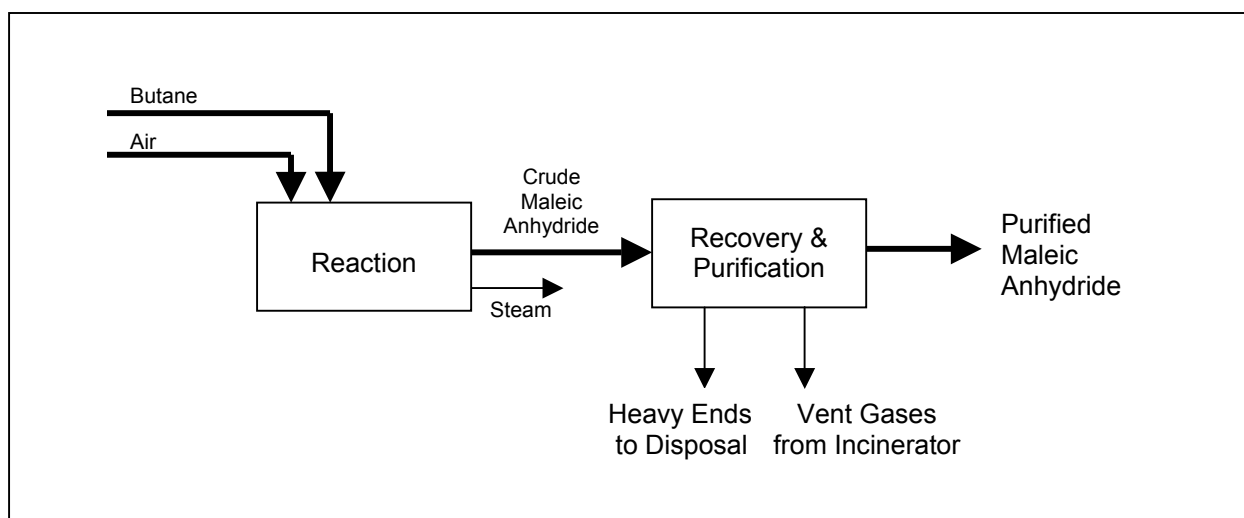


Salt bath coolers are used to cool the contents of the reactors and generate high-pressure steam. Heat exchangers cool the reaction product stream and generate medium pressure steam.

In the recovery and purification section, the reaction product passes through a phase separator. The gas stream from the separator is fed to the bottom of an absorber and flows counter current to the organic solvent. Overhead gases from the absorber are incinerated. (Fuel requirements for the incineration of the gases removed in the absorber are a significant part of the energy requirements for the maleic anhydride process and are considered in each energy level.) The liquid effluent from the absorber, consisting of solvent and maleic anhydride, is fed to a stripper. In the stripper, crude maleic anhydride is removed overhead. Solvent from the bottom of the stripper is recycled to the absorber, with a small portion pumped to the thin film evaporator for purification. The crude liquid maleic anhydride from the stripper and the phase separator is purified by distillation in a series of two columns.

Figure 6. Base Process for Maleic Anhydride Production

From n-butane via fixed bed with organic solvent recovery



Energy Performance Levels

A summary of the energy performance levels for maleic anhydride is given in Table 17. Subsequent sections describe the determination of each level.

Table 17. Energy Performance Levels for the Production of Maleic Anhydride
Energy requirements in BTU per pound of product.

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	Level 1	Level 2	Level 3	Level 4
Electricity Requirement	1,421	1,421	1,421	1,271	
Hot Utility Requirement	2,857	1,312	901	1,487	
Auxiliary Fuel Requirements for Incineration	3,227	3,227	3,227	252	
Hot Utility Credit	-6,698	-6,698	-6,698	-10,263	
Net Power & Hot Utility Requirements	807	-738	-1,149	-7,253	
Fuel Energy for Electricity Generation	4,581	4,581	4,581	4,097	
Fuel Energy for Steam/Heat Transfer Fluid	5,036	2,249	1,574	2,711	
Auxiliary Fuel Requirements for Incineration	3,227	3,227	3,227	252	
Total Fuel Energy Required	12,844	10,057	9,382	7,060	
Fuel Energy Credit	-12,077	-12,077	-12,077	-19,487	
Net Fuel Energy Consumed in Process	767	-2,020	-2,695	-12,423	-5,522
Raw Material Energy Consumed in Process	15,025	15,025	15,025	19,812	5,522
Total Energy Consumed in Process	15,792	13,005	12,330	7,389	0
Total Energy Consumed in Feedstock Production*	22,904	22,904	22,904	27,737	0
Total Energy Consumed in Product Chain	38,696	35,909	35,234	35,126	0

*Estimated with life cycle information for maleic anhydride. Information specifically for n-butane was not available.

Level 0---Base Process: From n-butane via fixed bed reactor and organic solvent recovery using dibutylphthalate as the solvent.

Level 1---Benchmarked Heat Integration: Base process is improved with addition of one process stream heat exchanger and the substitution of dibutyl hexahydrophthalate as the solvent in the recovery process

Level 2---Optimum Heat Integration: Base process is further improved with the addition of two more process stream heat exchangers.

Level 3---Process Redesign: From n-butane via fluidized bed, organic solvent recovery using dibutyl hexahydrophthalate as the solvent, one process stream heat exchanger, and additional steam generation.

Level 4---Theoretical Energy Requirement with 100% conversion of n-butane and 100% selectivity to maleic anhydride. The Gibbs free energy for the ideal reaction is -5,582 BTU/lb of product.

Level 0: Energy Requirements for the Base Case

Table 18 below summarizes the energy requirements for the base case. The air compressor for the air feed to the reactors takes approximately 90 percent of the electricity required for this process and 32 percent of the total fuel energy for the process. The major heat requirement occurs in the recovery section, where the heat required for the stripper reboiler constitutes approximately 47 percent of the total heat required for the

process (20 percent of the total fuel energy for the process). Fuel energy is credited for the steam generated in the reactor cooler and in the reactor product cooler.

Table 18. Level 0 Energy Requirements for Maleic Anhydride Production

Base Case: From n-butane via fixed bed with dibutylphthalate solvent.

Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	Total Process
Electricity Requirement	1,377	44	1,421
Hot Utility Requirement	411	2,446	2,857
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
Hot Utility Credit	-6,698	0	-6,698
Net Power & Hot Utility Requirements	-4,910	5,717	807
Fuel Energy for Electricity Generation	4,439	142	4,581
Fuel Energy for Steam/Heat Transfer Fluid	675	4,361	5,036
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
<u>Total Fuel Energy Required</u>	5,114	7,730	12,844
Fuel Energy Credit	-12,077	0	-12,077
Net Fuel Energy Consumed by Process	-6,963	7,730	767

Level 1: Energy Requirements for the Benchmarked Heat Integration Case

The maleic anhydride process given in PEP Review 93-2-3 includes two improvements to the base case that result in energy savings in the recovery section of the process. The first improvement is a process stream heat exchanger which uses the hot stripper bottom stream, which must be cooled before being recycled to the absorber, to heat the cold feed to the stripper. This heat exchanger results in fuel energy savings of 949 BTUs per pound of maleic anhydride.

Table 19. Level 1 Energy Requirements for Maleic Anhydride Production

Benchmarked Heat Integration: From n-butane via fixed bed with dibutyl

hexahydrophthalate solvent and one process stream heat exchanger.

Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	Total Process
Electricity Requirement	1,377	44	1,421
Hot Utility Requirement	411	901	1,312
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
Hot Utility Credit	-6,698	0	-6,698
Net Power & Hot Utility Requirements	-4,910	4,172	-738
Fuel Energy for Electricity Generation	4,439	142	4,581
Fuel Energy for Steam/Heat Transfer Fluid	675	1,574	2,249
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
<u>Total Fuel Energy Required</u>	5,114	4,943	10,057
Fuel Energy Credit	-12,077	0	-12,077
Net Fuel Energy Consumed by Process	-6,963	4,943	-2,020

The second improvement is the use of dibutyl hexahydrophthalate as the solvent, in place of dibutyl phthalate. According to the PEP report, the cost of using dibutyl hexahydrophthalate is approximately the same as that of using dibutyl phthalate. However, the amount of dibutyl hexahydrophthalate required to absorb maleic anhydride from the reactor effluent is one quarter to one third of the amount of dibutyl phthalate that is required, and according to process simulation results, the amount of energy saved when dibutyl hexahydrophthalate is used is approximately 968 BTU per pound of product (1838 BTU of fuel energy per pound of product). Level 1 energy requirements are summarized in Table 19. Compared to the Level 0 base case, they constitute 22% savings in the total fuel energy required.

Level 2: Energy Requirements for Optimum Heat Integration

Process Stream Heat Exchangers

The oxidation of n-butane to form maleic anhydride and the side reactions that form carbon monoxide and carbon dioxide are exothermic reactions. Much of the heat generated in the reactor is recovered in the base case design in the form of steam. The PEP benchmark case incorporates the most significant heat exchanger between process streams. This heat exchanger exchanges the hot stripper bottom stream, which must be cooled before entering the absorber, with the cold feed to the stripper, resulting in a fuel energy savings of 949 BTU per pound of product.

Pinch analysis shows that two additional opportunities for process stream heat exchangers exist in the process. Heat removed from the partial condenser can provide the heat necessary for both the air heater and the butane vaporizer, eliminating the need for steam heating in the reaction section and saving 675 BTU of fuel energy per pound of product.

Heat Pumps

Heat pumps are not applicable to this process. Once the opportunities for heat exchange have been identified, the remaining streams are poor candidates for heat pumps due to the small amount of heat available for transfer and the large temperature shifts that would be required.

Table 20 below gives a summary of the energy requirements for Level 2, which constitute a 27% savings in fuel energy required from the base process and 5% savings from Level 1.

Table 20. Level 2 Energy Requirements for Maleic Anhydride Production

Optimum Heat Integration: From n-butane via fixed bed with dibutyl hexahydrophthalate solvent and three process heat exchangers.

Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	Total Process
Electricity Requirement	1,377	44	1,421
Hot Utility Requirement	0	901	901
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
Hot Utility Credit	-6,698	0	-6,698
Net Power & Hot Utility Requirements	-5,321	4,172	-1,149
Fuel Energy for Electricity Generation	4,439	142	4,581
Fuel Energy for Steam/Heat Transfer Fluid	0	1,574	1,574
Auxiliary Fuel Requirements for Incin.	0	3,227	3,227
<u>Total Fuel Energy Required</u>	<u>4,439</u>	<u>4,943</u>	9,382
Fuel Energy Credit	-12,077	0	-12,077
Net Fuel Energy Consumed by Process	-7,638	4,943	-2,695

Level 3: Energy Requirements for Process Redesign

Selected Option for Level 3

The process redesign option chosen for Level 3 is in the category of *Unit Operation Design*.

Reactor operating conditions can have a significant impact on the energy efficiency of the maleic anhydride process. Reactor operating temperature and the homogeneity of that temperature can both affect energy efficiency by influencing product yield. The main reactions involved in the synthesis of maleic anhydride from butane were noted earlier (Equations 5 through 8). As temperature is increased, the conversion of n-butane increases, but the selectivity to maleic anhydride decreases. This results in a maximum in yield. The temperature at which this maximum occurs is dependent on the specific catalyst formulation; however, simulations performed by students at the University of Texas indicate that differences in yield over a 5-10°C temperature range are approximately 5%. Since overall yields of maleic anhydride from butane are on the order of 50%, this means that lack of adequate temperature control in the reactor would lead to a 10% change in energy requirements per pound of maleic anhydride produced, not accounting for the lost butane (if the unreacted butane is incinerated along with the by-product CO, then the energy value of the unreacted butane can be recovered by reducing supplemental natural gas feed to the incinerator).

Several approaches have been adopted for maintaining temperature control in the reactor for the maleic anhydride process. One approach involves controlling water content in the feed and adding a phosphate compound. The phosphate can broaden reactor hot spots, making the reactor more isothermal (references 548158, 548164, 548148 from the PEP

Review 93-2-3). An alternative approach is to change the reactor configuration. A two stage reactor (PEP reference 548155), a thin, flat, layered catalyst bed that improves heat transfer (PEP reference 548167) and fluidized bed or moving bed designs have all been suggested.

Process redesigns were evaluated for a fluidized bed reactor and for a fixed bed reactor using graded, shaped catalysts and an alkyl phosphate catalyst promoter. The fluidized bed design yielded the lowest net fuel energy consumed and the lowest total energy consumed of the redesign options considered.

Fluid bed reactors promote isothermal operation and allow for higher butane concentrations in the reactor feed. PEP Review 94-2-3²⁴ gives a production process for maleic anhydride via a fluidized bed reactor and an organic solvent absorber system. Energy requirements for this process are summarized below in Table 21. The process shows a 45% saving in total fuel energy required, compared to the Level 0 base case, and a 61% increase in fuel energy credit. This process consumes more butane per pound of maleic anhydride produced that does the base case, however the total energy consumed by the process is still 40% less than that of Level 2, as shown in Table 22.

The overall yield of maleic anhydride is reported to be 46 percent based on n-butane, which is considerably lower than the fixed bed process, for which the overall yield was 58.7 percent. The fluidized bed design results in a higher net production of energy however, mainly because the waste gas stream, which has a higher butane concentration in this process, is not incinerated, but is used as fuel to generate additional steam. Energy requirements for air compression are also less in the fluid bed process. The process configuration for Level 3 is very similar to that shown in Figure 6.

From PEP Reviews 93-2-3 and 94-2-3, the estimated total fixed capital cost for the fluidized bed process is 29 percent lower than the estimated total fixed capital cost for the fixed bed process, based on the same plant capacity and cost basis. The product value for the fluidized bed process is estimated to be \$0.4762 per pound of product as compared to \$0.6194 per pound for the base process.

Table 21. Level 3 Energy Requirements for Maleic Anhydride Production

Process Redesign: Fluid-bed process with additional steam generation

Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	Total Process
Electricity Requirement	1,154	117	1,271
Hot Utility Requirement	0	1,487	1,487
Auxiliary Fuel Requirements for Incin.	0	252	252
Hot Utility Credit	-7,077	-3,186	-10,263
Net Power & Hot Utility Requirements	-5,923	-1,329	-7,252
Fuel Energy for Electricity Generation	3,719	378	4,097
Fuel Energy for Steam/Heat Transfer Fluid	0	2,711	2,711
Auxiliary Fuel Requirements for Incin.	0	252	252
<u>Total Fuel Energy Required</u>	3,719	3,341	7,060
Fuel Energy Credit	-13,430	-6,047	-19,487
Net Fuel Energy Consumed by Process	-9,711	-2,706	-12,423

Table 22. Comparison of Energy Requirements for Maleic Anhydride Levels 2 and**3**

Energy requirements in BTU per pound of maleic anhydride.,

	Level 2	Level 3
Electricity Requirement	1,421	1,271
Hot Utility Requirement	901	1,487
Auxiliary Fuel Requirements for Incin.	3,227	252
Hot Utility Credit	-6,698	-10,263
Net Power & Hot Utility Requirements	-1,149	-7,252
Fuel Energy for Electricity Generation	4,581	4,097
Fuel Energy for Steam/Heat Transfer Fluid	1,574	2,711
Auxiliary Fuel Requirements for Incin.	3,227	252
<u>Total Fuel Energy Required</u>	9,382	7,060
Fuel Energy Credit	-12,077	-19,487
Net Fuel Energy Consumed by Process	-2,695	-12,423
Raw Material Energy Consumed in Process	15,025	19,812
Total Energy Consumed in Process	12,330	7,389

Additional Options Considered for Level 3Unit Operation Design

The second reactor design that was evaluated was a fixed bed reactor using graded, shaped catalysts and an alkyl phosphate catalyst promoter. This design resulted in improvements in energy efficiency over Level 2, but was not as efficient as the fluid bed reactor.

PEP Review 93-2-3 also offers a process design for production of maleic anhydride that incorporates shaped catalysts in a fixed bed that is graded with respect to catalyst activity, and an alkyl phosphate catalyst promoter, which is continuously added to the reactor feed. The graded shaped catalyst bed operates at a higher temperature, pressure, and n-butane concentration than the base case. Conversion of n-butane is lower in this design than in the Level 1 case, but selectivity to maleic anhydride is higher, and the overall yield of maleic anhydride for the shaped catalyst bed is 60.4 mole percent as compared to 58.7 percent for the Level 1 benchmark case.

The energy requirements for the shaped catalyst bed are summarized in Tables 23 and 24. This design results in energy savings when compared to the Level 1 case, mainly because the waste gas stream created in the shaped catalyst bed design is of lower volume and greater butane concentration and requires less fuel to incinerate. Total fuel energy required is reduced by 46% from the Level 0 base case, although the fuel energy credit is also reduced by 12%. The net fuel energy consumed by the process is less than that for Level 2, but is higher than the fluid-bed design.

Table 23. Alternate Unit Operation Design Considered for Level 3 for Maleic Anhydride

Process Redesign: Graded, Shaped Catalysts and Alkyl Phosphate Catalyst Promoter,
Fixed bed reactor, organic solvent recovery
Energy requirements in BTU per pound of maleic anhydride.

	Reaction Section	Recovery & Purification Section	Total Process
Electricity Requirement	1,452	42	1,494
Hot Utility Requirement	173	886	1,059
Auxiliary Fuel Requirements for Incin.	0	265	265
Hot Utility Credit	-5,843	0	-5,843
Net Power & Hot Utility Requirements	-4,218	1,193	-3,025
Fuel Energy for Electricity Generation	4,680	135	4,815
Fuel Energy for Steam/Heat Transfer Fluid	285	1,557	1,841
Auxiliary Fuel Requirements for Incin.	0	265	265
<u>Total Fuel Energy Required</u>	<u>4,965</u>	<u>1,957</u>	6,922
Fuel Energy Credit	-10,579	0	-10,579
Net Fuel Energy Consumed by Process	-5,614	1,956	-3,658

Table 24. Comparison of Shaped Catalyst Fixed Bed Option with Level 2 and Level 3
Energy requirements in BTU per pound of maleic anhydride.

	Level 2	Shaped Catalysts Fixed Bed Reactor	Fluid Bed Reactor (Level 3)
Electricity Requirement	1,421	1,494	1,271
Hot Utility Requirement	901	1,059	1,487
Auxiliary Fuel Requirements for Incin.	3,227	265	252
Hot Utility Credit	-6,698	-5,843	-10,263
Net Power & Hot Utility Requirements	-1,149	-3,025	-7,252
Fuel Energy for Electricity Generation	4,581	4,815	4,097
Fuel Energy for Steam/Heat Transfer Fluid	1,574	1,841	2,711
Auxiliary Fuel Requirements for Incin.	3,227	265	252
<i>Total Fuel Energy Required</i>	9,382	6,922	7,060
Fuel Energy Credit	-12,077	-10,579	-19,487
Net Fuel Energy Consumed by Process	-2,695	-3,658	-12,423

Recovery operating conditions could also have a significant impact on the energy efficiency of the maleic anhydride process. The main factors controlling energy efficiency in the separator design are the choice of absorbent (which is discussed in the section on material selection) and the balance between maleic anhydride loss from the absorbing column and the absorber flow rate.

Material Selection

The main material choice, beyond the feed materials (air and n-butane), that were considered fixed, was the organic absorbent. In the maleic anhydride process, the purpose of the absorbing liquid is to separate maleic anhydride from the other components of the cooled reactor effluent (CO, CO₂, H₂O, n-butane). This is not a particularly difficult separation, although some light gases and water will be absorbed along with the maleic anhydride. In a typical process configuration, the light gases are first flashed (with some loss of maleic anhydride), then contacted with the absorbing liquid. The absorbing liquid, containing the product maleic anhydride, is sent to a regeneration column where the maleic anhydride is volatilized, and the regenerated absorbing fluid is sent back to the absorbing column.

An ideal absorbent would have a high solubility for maleic anhydride, and its heat of vaporization would be optimized based on energy requirements and absorbent loss rates. A high heat of vaporization would minimize absorbent losses in the absorbing column, but would cause high reboiler duties in the regeneration column. Conversely, a low heat of vaporization would minimize reboiler duties in the regeneration column but might lead to excessive solvent losses.

Use of an improved solvent is incorporated in the PEP benchmark process (Level 1). The use of dibutyl hexahydrophthalate instead of dibutyl phthalate results in energy savings of 71 percent in the regeneration column reboiler and a 14 percent reduction in total fuel energy needed for the process.

Process Integration and Recycle Structure

The partial oxidation reaction of n-butane is typically run at a 50-60% yield. While some of the by-products are CO and CO₂, there is also a significant amount of unreacted n-butane. In the base case and in the shaped catalyst case this n-butane is sent to an incinerator which destroys CO and other undesired by products. In these instances, the n-butane displaces the need for some auxiliary fuel. In the fluidized bed case the unreacted n-butane is used as fuel to generate steam. As long as the n-butane is used to displace fuel that would otherwise be consumed, there is no direct energy penalty associated with burning the unreacted n-butane.

PEP Review 94-2-3 examines the option of using pressure-swing adsorption as the technology for recycling unreacted butane to the reactor. The reactor yield in this case increased to 66 percent, but butane savings are offset by lower steam credits, higher costs for supplemental fuel to incinerate waste gas and the energy requirement to compress the recycled butane. The option for recycling butane becomes more attractive economically for sites where butane costs are relatively high compared to utility costs.

Utility Design and Fluid Handling

Feed compression is the main energy sink in the fluid handling system. Energy requirements for compression constitute 32 percent of the total fuel energy requirements for the process. Catalyst types and arrangements that reduced the pressure drop in the reactor would provide another approach to reducing compression energy requirements.

Compression requirements are reduced in the fluid-bed process because the butane to air ratio of the feed is increased. The shaped catalyst fixed bed design also operates with a higher butane to air ratio than the base case, but compression requirements are higher in this design to compensate for the increased pressure drop in the reactor.

Level 4: Energy Requirements Based on Theoretical Minimum Energy

The heat of reaction for the ideal reaction at standard conditions is -5,522 BTU/lb maleic anhydride. The change in the Gibbs free energy of the ideal reaction at standard conditions is -5,582 BTU/lb of maleic anhydride.

3.4 Terephthalic Acid

Terephthalic acid ($C_6H_4-1,4-(CO_2H)_2$, CAS#100-21-0), or 1,4 benzene dicarboxylic acid, is used in the production of polyethylene terephthalate (PET), a common plastic used in bottle resin, films and fibers. Worldwide production of terephthalic acid is approximately 12 million tons (approximately 3 million tons per year in the U.S.).

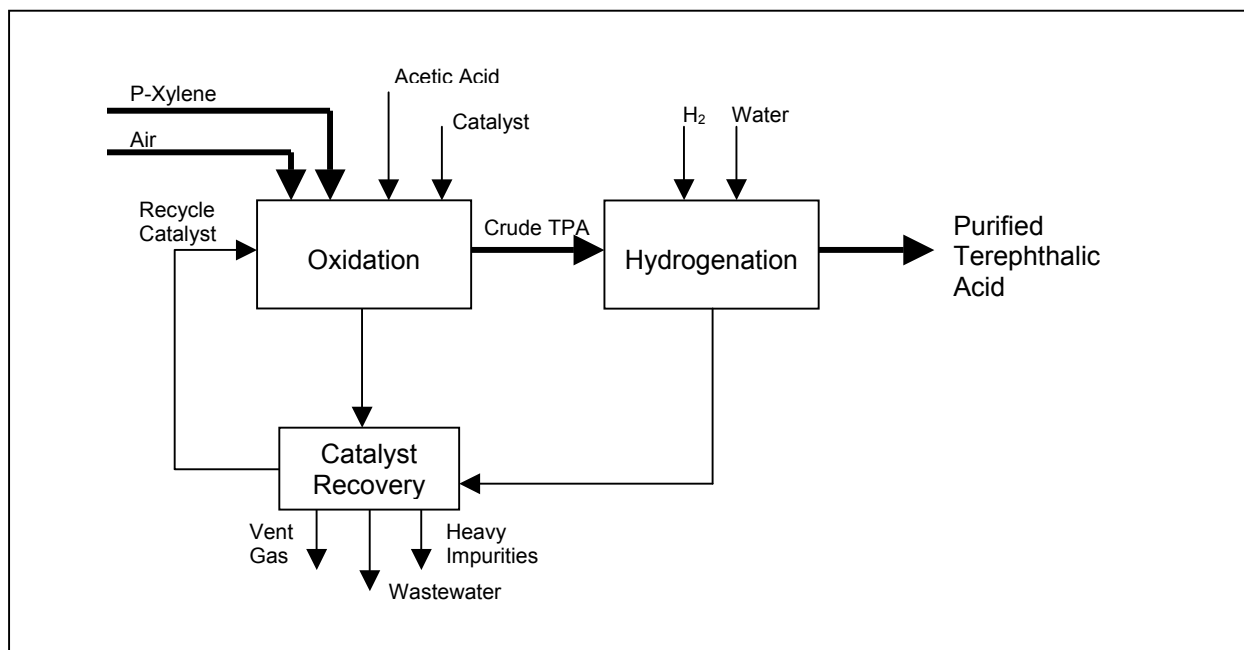
The Base Process

Terephthalic acid is primarily produced via the bromine catalyzed partial oxidation of p-xylene. The level of technological innovation and process change for terephthalic acid manufacturing has been greater than for many other processes, as documented in the extensive patent literature. The base case for this analysis will be the process technology in use in 1997, and is based on PEP Report 9e²⁵.

In the base case process, para-xylene is oxidized with air to terephthalic acid in the presence of a cobalt-manganese-bromine catalyst. As shown in Figure 7, the process consists of three major sections: the oxidation section, the hydrogenation section and the catalyst recovery section.

Figure 7. Base Process for Terephthalic Acid Production

From p-xylene via bromine-promoted air oxidation.

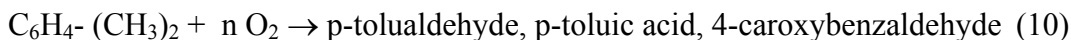


The oxidation reaction is performed in the liquid phase at approximately 150-200°C and 100-300 psia, in a stirred tank reactor, with an acetic acid solvent. The oxidation reaction proceeds through a number of intermediates, including para-toluic acid and 4-carboxybenzaldehyde.

The desired reaction is



The undesired reactions include:



After exiting the oxidation reactor, the crude terephthalic acid undergoes a series of flash crystallizations. The overhead product from the flash crystallizations contains acetic acid, by-products and some terephthalic acid. This stream is stripped and distilled to recover the acetic acid solvent, which is recycled to the reactor. The crude product is further refined in a series of water washes and is then sent to a hydrogenation reactor where some the remaining by-products are hydrogenated to improve their solubility. After hydrogenation, the refined product is washed, crystallized and dried.

In the catalyst recovery section, process vent gases and distillation residues are incinerated. Fly ash is collected in an electrostatic precipitator and treated to recover catalyst, which is recycled to the oxidation section. Combustion gases are scrubbed with process wastewater (condensed steam from the solvent evaporator). A gas vent stream, wastewater stream and residue waste streams are produced.

Energy Performance Levels

A summary of the energy performance levels for terephthalic acid is given in Table 25. Subsequent sections describe the determination of each level.

Table 25. Energy Performance Levels for the Production of Terephthalic Acid

Energy requirements in BTU per pound of product.

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	Level 1	Level 2	Level 3	Level 4
Electricity Requirement	600	600	600	815	
Hot Utility Requirement	3,200	2,366	2,366	5,238	
Fuel for Waste Incineration	373	373	373	874	
Electricity Credit	0	-73	-73	-618	
Hot Utility Credit	0	0	0	-3,399	
Net Power & Hot Utility Requirements	4,173	3,266	3,266	2,911	
Fuel Energy for Electricity Generation	1,934	1,934	1,934	2,627	
Fuel Energy for Steam/Heat Transfer Fluid	5,122	4,076	4,076	7,280	
Auxiliary Fuel Requirements for Incineration	373	373	373	874	
<u>Total Fuel Energy Required</u>	<u>7,429</u>	<u>6,382</u>	<u>6,382</u>	<u>10,783</u>	
Fuel Energy Credit	0	-235	-235	-7,355	
Net Fuel Energy Consumed in Process	7,429	6,148	6,148	3,426	-3,160
Raw Material Energy Consumed in Process	3,890	3,890	3,890	4,392	3,160
Total Energy Consumed in Process	11,319	10,038	10,038	7,818	0
Total Energy Consumed in Feedstock Production	17,594	17,594	17,594	18,338	0
Total Energy Consumed in Product Chain	28,913	27,632	27,632	26,156	0

Level 0: Base Case--from p-xylene via bromine-promoted air oxidation (Heat of reaction recovered in process stream heat exchanger.)

Level 1: Benchmarked Heat Integration Case—Base process is improved with two heat exchangers, power generation and heat transfer fluid heated in residue incinerator.

Level 2: Optimum Heat Integration—No further improvements are included.

Level 3: Process Redesign: From p-xylene by the hydrolysis of dimethyl terephthalate

Level 4: Theoretical energy requirement with 100 percent conversion of p-xylene and 100 percent selectivity to terephthalic acid. The Gibbs free energy for the ideal reaction is -3,051 BTU/lb terephthalic acid.

Level 0: Energy Requirements for the Base Case

Table 26 summarizes the energy requirements for the base case. Air compression for the air feed to the reactors takes approximately 20 percent of the total fuel energy for the process. The major heat requirement occurs in the hydrogenation section, where the heat required for the solvent evaporator reboiler takes approximately 34 percent of the total fuel energy for the process.

A fuel energy credit is not given for the base process because the heat of reaction is not converted to steam. The heat is recovered, however, by using the heat from the hot reactor product stream to drive the reboilers of the solvent dehydration column. This heat exchanger, which is included in the Level 0 energy requirements, saves approximately 3135 BTUs of fuel energy per pound of product, which would otherwise be needed to drive the reboilers.

Table 26. Level 0 Energy Requirements for Terephthalic Acid Production

Base Process: From p-xylene via bromine-promoted air oxidation.

Heat of oxidation reaction recovered by directly heating reboilers of solvent dehydration columns. Energy requirements in BTU per pound of product.

	Oxidation Section	Hydrogenation Section	Catalyst Recovery Section	Total Process
Electricity Requirement	505	53	42	600
Hot Utility Requirement	221	2,959	21	3,200
Fuel for Waste Incineration	0	0	373	373
Net Power & Hot Utility Requirements	726	3,012	436	4,173
Fuel Energy for Electricity Generation	1,627	172	135	1,934
Fuel Energy for Steam/Heat Transfer Fluid	409	4,681	33	5,122
Auxiliary Fuel Requirements for Incin.	0	0	373	373
<i>Total Fuel Energy Required</i>	2,036	4,852	540	7,429
Fuel Energy Credit	0	0	0	0
Net Fuel Energy Consumed in Process	2,036	4,852	540	7,429

Level 1: Energy Requirements for the Benchmarked Heat Integration Case

The terephthalic acid process given in PEP Report 9e includes three improvements to the base process which result in energy savings. The first improvement uses the nitrogen that is compressed in the air feed to the reactor to generate electricity. In this process, the uncondensed vapors from the reactor are scrubbed with water to remove acetic acid. Gases from the scrubber are sent to a Pressure Swing Absorption (PSA) unit that removes water and organic contaminants. The resulting stream of nitrogen is expanded to produce electricity and a stream of nitrogen for plant use. The electricity produced results in a fuel energy credit of 235 BTUs per pound of product.

A process stream heat exchanger is incorporated in the hydrogenation section, in which wash water used prior to final crystallization is heated with steam from the solvent evaporator overhead. Approximately 370 BTUs of fuel energy per pound of product are saved with this heat exchanger. The third improvement consists of using heat from the residue incinerator to provide some of the heat requirement for the heat transfer fluid. Heat transfer fluid is used in the hydrogenation section to heat the crude PTA slurry prior to entering the dissolver, and subsequently the hydrogenation reactor. This improvement results in fuel energy savings of approximately 789 BTUs per pound of product.

Compared to the Level 0, Level 1 requirements constitute 14% savings in total fuel energy required and with the additional power generation, 17% savings in net fuel energy consumed.

Table 27. Level 1 Energy Requirements for Terephthalic Acid Production

Benchmarked Heat Integration Case: From p-xylene via bromine-promoted air oxidation. The nitrogen stream from reactor vapors is expanded to produce electricity. Additional hot utility is required to heat the nitrogen for plant use. One heat additional heat exchanger is employed, and heat transfer fluid required is partially heated with heat from the residue incinerator. Energy requirements in BTU per pound of product.

	Oxidation Section	Hydrogenation Section	Catalyst Recovery Section	Total Process
Electricity Requirement	505	53	42	600
Hot Utility Requirement	292	2,053	21	2,366
Fuel for Waste Incineration	0	0	373	373
Electricity Credit	-73			-73
Net Power & Hot Utility Requirements	724	2,106	436	3,266
Fuel Energy for Electricity Generation	1,627	172	135	1,934
Fuel Energy for Steam/Heat Transfer Fluid	522	3,522	33	4,076
Auxiliary Fuel Requirements for Incineration	0	0	373	373
<u>Total Fuel Energy Required</u>	2,149	3,693	540	6,382
Fuel Energy Credit	-235	0	0	-235
Net Fuel Energy Consumed in Process	1,914	3,693	540	6,148

Level 2: Energy Requirements for Optimum Heat Integration

Process Stream Heat Exchangers

In the PEP benchmark case, the heat of reaction is used to supply energy to the solvent dehydration column. The other significant opportunity for heat integration is also included in the benchmark case, which is the use of heat from the solvent evaporator overhead to heat the wash water used prior to final crystallization. Once these opportunities for heat exchange have been used, there are only two significant cold streams remaining in the process. The temperatures of the remaining heat sources are not high enough to enable heat exchange with these cold streams.

Heat Pumps

The two remaining cold streams in the process cannot be practically heated with heat pumps. Process stream combinations do not meet the prerequisites for further investigation of heat pumps for this process.

The Level 2 requirements are therefore identical to the energy requirements for the PEP Benchmark case (Level 1).

Level 3: Energy Requirements for Process Redesign

Selected Option for Level 3

The process redesign option chosen for Level 3 is in the category of *Unit Operation Design*. Level 3 energy requirements are based on a process design for producing terephthalic acid from p-xylene by the hydrolysis of dimethyl terephthalate (DMT). The design is presented in PEP Review 96-10²⁶ and is predominantly based on a Huls patent (US 5,338,882)

As shown in Table 28, the electricity and hot utility requirements are actually higher for this process configuration than for the base process. The fuel energy credit generated by the process, however, offsets these higher requirements, resulting in a net fuel energy consumed in the hydrolysis of DMT that is 54 percent lower than the net fuel energy consumed in the base process.

Table 28. Level 3 Energy Requirements for Terephthalic Acid Production
Process Redesign: From p-xylene by the hydrolysis of dimethyl terephthalate
Energy requirements in BTU per pound of product.

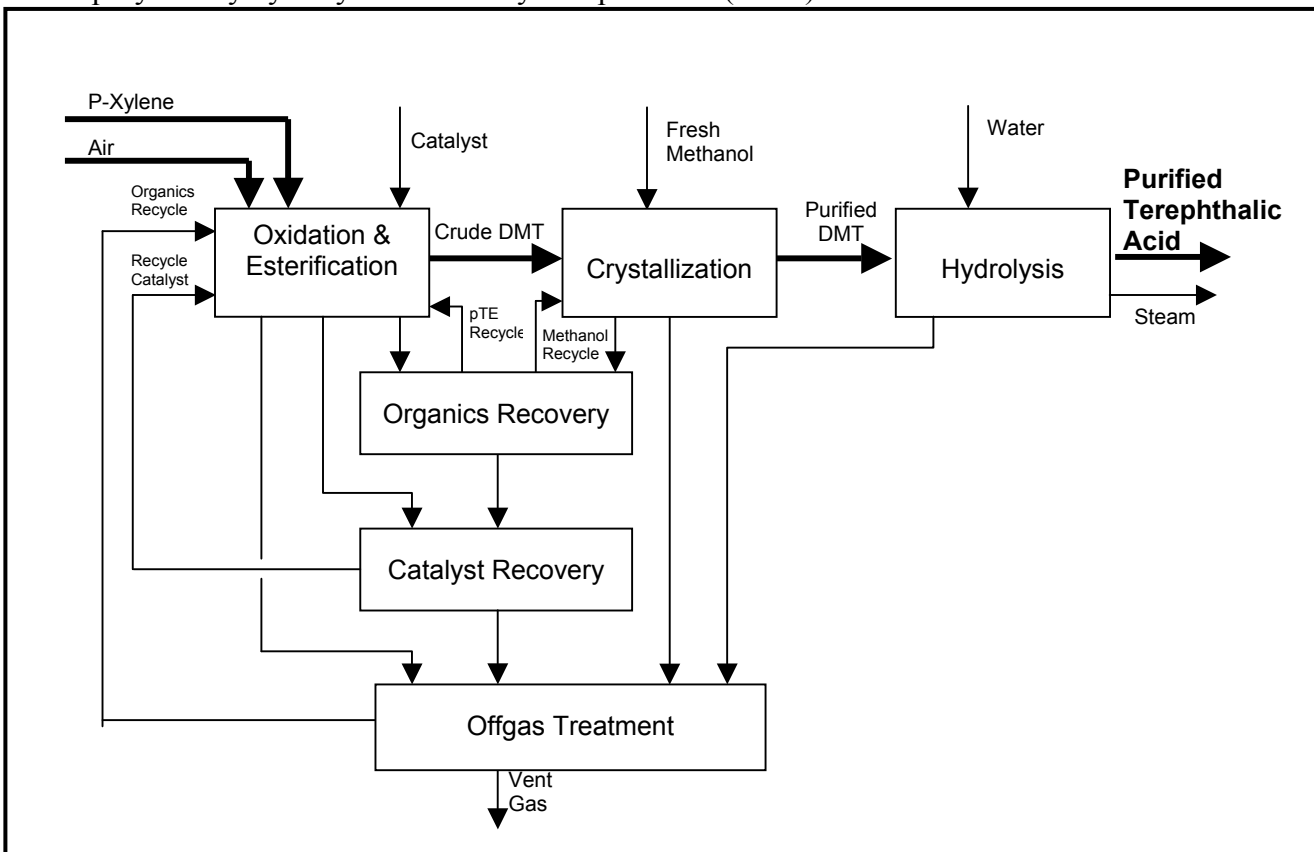
	Oxidation & Esterifi- cation	Crystalliza- tion	Organics Recovery	Catalyst Recovery	Offgas Treatment	Hydro- lysis	Total Process
Electricity Requirement	13	54	6	2	699	41	815
Hot Utility Requirement	1,380	1,039	874	4	0	1941	5,238
Fuel for Waste Incineration	0		0	0	874	0	874
Electricity Credit	0		0	0	-618	0	-618
Hot Utility Credit	-1,119		0	0	0	-2280	-3,399
Net Power & Hot Utility Requirements	274	1,093	879	6	955	-297	2,911
Fuel Energy for Electricity Generation	43	174	18	5	2,253	134	2,627
Fuel Energy for Steam/Heat Transfer Fluid	1,687	1,686	1,329	6	0	2,571	7,280
Auxiliary Fuel Requirements for Incineration	0	0	0	0	874	0	874
Total Fuel Energy Required	1,730	1,860	1,347	11	3,127	2,705	10,783
Fuel Energy Credit	-1,666	0	0	0	-1,993	-3,696	-7,355
Net Fuel Energy Consumed in Process	64	1,860	1,347	11	1,134	-991	3,426

Comparison of the product values for PTA produced by the two processes given in PEP Review 96-10 shows the product value for the Level 3 process to be slightly lower than that for the base case. The product value is \$0.4942 for the Level 3 process (Huls hydrolysis of DMT) and \$0.5081 for the base case (bromine promoted oxidation). The Level 3 process has slightly higher capital-related costs, but lower variable costs than the base case process.

The Level 3 process is described below. As shown in Figure 8, the process has six major sections.

Figure 8. Process Redesign for Terephthalic Acid Production

From p-xylene by hydrolysis of dimethyl terephthalate (DMT)



In the oxidation section, p-xylene is oxidized with air to p-toluic acid over a cobalt-manganese catalyst. Simultaneously, recycled methyl p-toluate (pTE) is oxidized to monomethyl terephthalate. The product is esterified with methanol and distilled to produce recycle pTE, dimethyl terephthalate (DMT), catalyst-containing residue, and pTE-containing methanol vapor.

In the crystallization section, the crude DMT is purified by crystallization from methanol. The filtrate is concentrated and recrystallized to produce methanol vapor, additional DMT, and an isomers-containing waste stream.

Pure DMT from crystallization is hydrolyzed with water in the hydrolysis section to produce terephthalic acid, which is purified by crystallization from water. The methanol produced by hydrolysis is purified and recycled to DMT crystallization. Steam (275 psig and 90 psig) generated by the heat produced in the hydrolysis reactor is in excess of quantities required by the process and is credited as export steam.

Catalyst containing residue is transesterified with methanol to recover pTE and other components for recycle to oxidation. Various process streams are distilled to produce pure methanol, which is recycled to the crystallization section. Catalyst is recovered from the residue in the catalyst recovery section by liquid-liquid separation and ion-exchange.

In the offgas treatment section the oxidation offgas is scrubbed to recover organic components for recycle, then incinerated, along with essentially all other process waste streams. The furnace offgas is used to generate process heat and to turn a turbine that powers the oxidation air compressors.

Additional Options Considered for Level 3

Material selection

Pure oxygen, rather than air, can be used as a feed material (US patents 5,371,283 and 5,696,285 to Praxair). The use of pure oxygen significantly reduces the amount of gas to be compressed. In addition, it allows the reactor to be operated at lower temperature and pressure. Nevertheless, the energy saving obtained in the compression step is offset by the relatively large amount of energy consumed for oxygen purification (presumably via cryogenic process). Similarly, the energy saving in compression obtained from the use of enriched air (e.g. 30% oxygen) is also easily offset by the energy required to produce the enriched air feed.

However, the use of pure oxygen or enriched air also improves the mass transfer in the reactor. Consequently, less of the undesired products are produced; leading to lower separation cost. The energy saving associated with the lower separation requirement may make the use of pure oxygen or enriched air more desirable. However, this energy saving could not be estimated with the available information.

The other primary material choice is the catalyst/promoter system. While there appear to be variations in the precise composition of the catalyst and promoters, as reported in the patent literature, these slight variations are unlikely to have a dramatic impact on process energy requirements.

Unit operation design

Reactor design: An Amoco patent (GB 1,555,246) reports an improved efficiency associated with a two stage reactor. The first stage in the two-stage reactor is operated in the same manner as the base case reactor. The secondary reactor is a combined oxidation reactor and crystallizer. According to the PEP report, this improves yield by approximately 5%. This is included in the base case.

Separation network--use of NMP Solvent: U.S. Patent 5,840,968 (HFM International, November, 1998) describes a process for generating pure terephthalic acid from the effluent of the oxidation reactor in one set of separation processes. This is in contrast to the base case process, where the separation occurs through a series of water washes, with intermediate hydrogenation.

The proposed process employs n-methyl pyrrolidone (NMP, recommended in U.S. Patent 5,961,935) or dimethyl acetamide (DMAC) as the solvent. An updated patent by the same group (U.S. Patent 6,054,610, April, 2000) expands the range of solvents covered. Although the use of NMP would result in major simplification of the separation process, it does not eliminate the need for major energy consuming unit operations in the process. In fact, the amount of NMP required is about twice the amount of acetic acid solvent used in the PEP base case. As solvent purification constitutes a significant portion of the total energy use, the use of NMP is not likely to result in energy savings.

Process integration and recycle structure

Among the streams generated in the base case process is carbon dioxide containing off-gases from the first oxidation reactor. U.S. Patent 5,693,856 suggests separating carbon dioxide from the reactor off-gas, using an absorbing column (using ethanolamines) or an adsorption column (using a zeolite). The captured carbon dioxide is then recycled to the reactor, reducing explosion hazard, if the reactor is operated with pure oxygen, and improving selectivity to terephthalic acid to 97%.

Another option for improving mass integration is to contact the aqueous phase from the crystallization units after hydrogenation (i.e. “pure plant mother liquor”) with p-xylene (U.S. patent 6,143,926, DuPont). p-Toluic acid would absorb into the organic phase which is recycled to the oxidation reactor. However, the concentration of p-toluic acid in the PEP benchmark case is relatively low. Therefore, recycling p-toluic acid to the oxidation reactor would have very small impact on the material intensity (reducing p-xylene requirement by less than 1%). It would also have very small impact on the energy requirement.

Still another innovation described in the patent literature is to take the effluent from the water wash after the flash crystallizations and to recycle this to the oxidation reactor (U.S. Patent RE36,008, December, 1998). This improvement is included in the base case process.

Utility design and fluid handling

Feed compression is a major energy sink in the fluid handling system. As discussed above, energy savings could be realized in this process if pure oxygen were used instead of air; however, overall energy requirements for producing the product would increase.

Level 4: Theoretical Energy Requirements

The heat of reaction for the ideal reaction at standard conditions is -3,160 BTU/lb of terephthalic acid. The change in Gibbs free energy of the ideal reaction at standard conditions is -3,051 BTU per pound of terephthalic acid.

3.5 Caprolactam

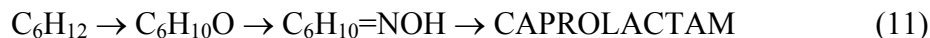
Caprolactam ($\text{C}_6\text{H}_{10}\text{NH}(\text{O})$), CAS#105-60-2), or 2-oxohexamethyleneimine, is used exclusively in the production of nylon, which is used as a fiber in carpets, textiles, and other products. Worldwide production of caprolactam is approximately 5 million tons (approximately 1 million tons per year in the U.S.).

Caprolactam is produced via a variety of technologies, using a range of feedstocks. Process feedstocks include butadiene, toluene, and phenol, but the most common route involves cyclohexane as a feed. The base case for this analysis will be the cyclohexanone oxime rearrangement chemistry.

The Base Process

In the base process, cyclohexane is oxidized with air to produce cyclohexanone. The cyclohexanone oxime is produced from cyclohexanone and hydroxylamine sulfate. The cyclohexanone oxime undergoes molecular rearrangement in the presence of oleum to produce crude caprolactam. A by-product stream of ammonium sulfate is produced during the neutralization of oleum. The process is based on Section 6 of PEP Report 41B, *Caprolactam from Cyclohexane, Nitric Oxide Hydrogenation*²⁷. Design information for this report is drawn mainly from patents assigned to BASF.

The desired reaction pathway is:



The undesired reactions include the formation of cyclohexanol in the production of cyclohexanone, and the production of ammonium sulfate as a by-product.

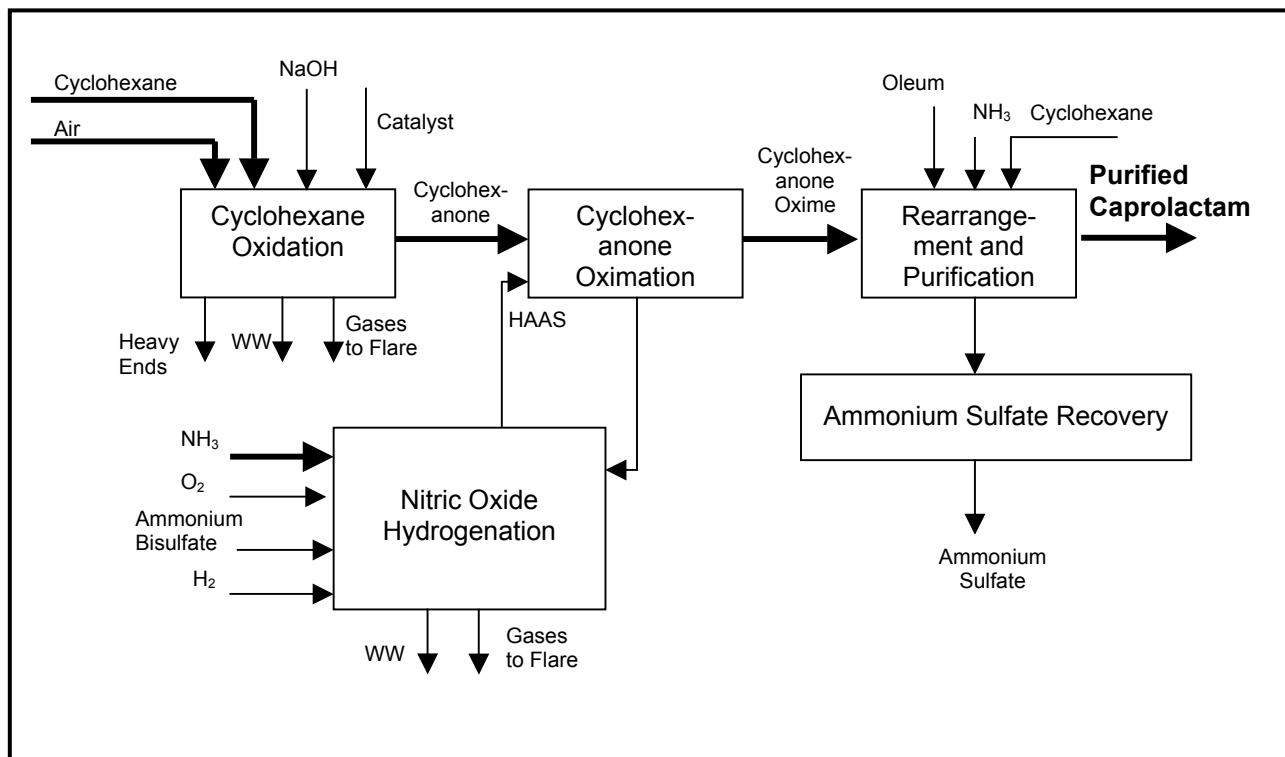
As shown in Figure 9, the major sections in the process flowsheet are cyclohexane oxidation, nitric oxide hydrogenation, cyclohexanone oximation, rearrangement and purification, and ammonium sulfate recovery.

Cyclohexane Oxidation Section: Liquid cyclohexane undergoes scrubbing and stripping pretreatment to remove water. It is then oxidized with air in a series of reactors. Part of the heat of oxidation is used to heat the air to the reaction temperature. The remaining heat is removed through the reactor cooling jackets where steam is generated.

The liquid oxidation product passes through a decomposition column, where it is treated with sodium hydroxide to convert cyclohexyl hydroperoxide into cyclohexanol and cyclohexanone. The organic product from the decomposition column is distilled to remove cyclohexane, which is recycled to the pretreatment stripper. The organic product is then saponified with caustic soda solution.

Figure 9. Base Process for Caprolactam production.

From cyclohexane via oxidation, nitric oxide hydrogenation, cyclohexanone oximation and Beckman rearrangement



The product leaving the top of the saponification column, rich in cyclohexanol and cyclohexanone, is treated in a washing column and then a dehydration column, where water and cyclohexane are removed. The washed product is distilled in a series of two columns to yield cyclohexanone. The cyclohexanol obtained in the bottom stream is further purified by distillation, dehydrogenated to cyclohexanone, and recycled to the dehydration column.

Nitric Oxide Hydrogenation Section: Evaporated ammonia is mixed with oxygen and then steam before being charged to a converter to produce nitric oxide. The reactor effluent is cooled by two heat exchangers, one that vaporizes the water for the reaction and another that generates additional steam. Most of the water in the reactor effluent is condensed and discharged. The reactor effluent gases are fed to an absorber and scrubbed with a cold nitric acid solution.

The gas leaving the top of the absorber, containing mostly nitric oxide, is sent to the hydroxylamine reactor, where nitric oxide is hydrogenated in the presence of an ammonium sulfate buffer solution to form hydroxylammonium-ammonium sulfate (HAAS).

The liquid HAAS product from the hydroxylamine reactor is passed through a centrifuge and filter to recover any residual catalyst. It is then treated in the decomposer reactor, which is designed to decompose small amounts of extra ammonium sulfate.

Cyclohexanone Oximation Section: HAAS solution is fed near the top of the oximation reactor and cyclohexanone is fed at the bottom of the reactor. The oxime reaction product drawn from the top of the reactor is fed to the postoximation reactor.

Spent HAAS solution from the bottom of the oximation reactor is extracted with cyclohexanone to remove the oxime. The cyclohexanone extract from the top of the column is used for the oximation reactor. The solution from the bottom of the column containing oxime and cyclohexanone is stripped to decompose the oxime to HAAS and cyclohexanone. Recovered cyclohexanone is used in the extraction column and the HAAS-lean buffer solution is recycled to the Nitric Oxide Hydrogenation Section for hydroxylamine production.

Rearrangement and Purification Section: Cyclohexane oxime is mixed with cyclohexane and a stream of caprolactam-containing oleum, and fed to the rearrangement reactor.

The reaction product passes through a decanter. The solvent phase, made up primarily of cyclohexane is circulated back to the rearrangement reactor. The caprolactam-oleum layer is neutralized with ammonia water to liberate caprolactam.

The neutralized mixture undergoes phase separation in a decanter. The aqueous layer, containing ammonium sulfate and some caprolactam is extracted with benzene in the ammonium sulfate recovery column. The bottom stream is sent to the Ammonium Sulfate Recovery Section. The benzene extract from the top of the column is sent to the bottom of the benzene extraction column, where the crude caprolactam layer from the decanter flows downward countercurrently with the benzene.

The crude caprolactam in benzene solution is withdrawn from the top of the column and distilled to yield the caprolactam-finished product. Distillation residue is fed to a thin film evaporator where crude caprolactam is recovered and recycled to the caprolactam distillation column.

Residue from the thin film evaporator is sent to a second thin film evaporator. The evaporated caprolactam is distilled in two stirred kettles and recycled to the benzene extraction column.

Ammonium Sulfate Recovery Section: Ammonium sulfate from the ammonium sulfate recovery column is sent to a crystallizer where most of the water is evaporated and part of the sulfate is crystallized. The sulfate slurry from the crystallizer is thickened and passed through a centrifuge. The sulfate wet cake from the centrifuge is dried with air.

The dried ammonium sulfate is transferred to a feed hopper, screened and packed into bags. Oversized ammonium sulfate is pulverized and recycled to the hopper.

Energy Performance Levels

A summary of the energy performance levels for caprolactam is given in Table 29. Subsequent sections describe the determination of each level.

Table 29. Energy Performance Levels for the Production of Caprolactam

Energy requirements in BTUs per pound of product.

	Base Process	Heat Integration Improvements		Process Redesign	Theoretical Energy
	Level 0	Level 1	Level 2	Level 3	Level 4
Electricity Requirement	963	963	1,032	827	
Hot Utility Requirement	16,500	16,500	14,581	9,023	
Auxiliary Fuel Requirements for Incineration	357	357	357	204	
Hot Utility Credit	-2,910	-2,910	-2,910	-2,758	
Net Power & Hot Utility Requirements	14,911	14,911	13,060	7,296	
Fuel Energy for Electricity Generation	3,105	3,105	3,326	2,666	
Fuel Energy for Steam/Heat Transfer Fluid	26,069	26,069	23,226	17,137	
Auxiliary Fuel Requirements for Incineration	357	357	357	204	
<u>Total Fuel Energy Required</u>	<u>29,531</u>	<u>29,531</u>	<u>26,909</u>	<u>20,008</u>	
Fuel Energy Credit	-4,307	-4,307	-4,307	-4,083	
Net Fuel Energy Consumed in Process	25,224	25,224	22,603	15,925	-2,133
Raw Material Energy Consumed in Process	10,581	10,581	10,581	7,576	2,133
Total Energy Consumed in Process	35,805	35,805	33,184	23,501	0
Total Energy Consumed in Feedstock Production	36,910	36,910	36,910	33,225	0
Total Energy Consumed in Product Chain	72,715	72,715	70,094	56,726	0

Level 0: Base Case--From cyclohexane via oxidation, nitric oxide hydrogenation, cyclohexanone oximation and Beckman rearrangement

Level 1: Benchmarked Heat Integration Case—No improvements are added to the base process.

Level 2: Optimum Heat Integration—Four process stream heat exchangers and one heat pump are added to the base process.

Level 3: Process Redesign-- From cyclohexane via oxidation (hydroperoxide process), nitric oxide hydrogenation, cyclohexanone oximation and Beckman rearrangement plus four process stream heat exchangers and one heat pump.

Level 4: Theoretical Energy Requirement with 100% conversion of cyclohexane and ammonia and 100% selectivity to caprolactam. The Gibbs free energy for the ideal reaction is -2,068.

Level 0: Energy Requirements for the Base Case

Energy requirements for the base case are summarized in Table 30 below. The most energy intensive section of the process is the oxidation of cyclohexane. The distillation columns in this section which separate cyclohexane from the organic reaction products consume over 50 percent of the fuel energy required for the entire caprolactam process. Fuel energy is credited for the steam produced by cooling the oxidation reactors and for the steam produced by cooling the converter in the nitric oxide hydrogenation section.

Table 30. Level 0 Energy Requirements for Caprolactam Production

Base case: From cyclohexane via oxidation, nitric oxide hydrogenation, cyclohexanone oximation and Beckman rearrangement.

Energy requirements in BTU per pound of product.

	Oxidation	Hydrogenation	Oximation	Rearrangement & Purification	NH ₃ SO ₄ Rec.	Total Process
Electricity Requirement	313	260	3	342	45	963
Hot Utility Requirement	11,907	8	1,423	1,095	2,067	16,500
Auxiliary Fuel Requirements for Incineration	357	0	0	0	0	357
Hot Utility Credit	-1,839	-1,071				-2,910
Net Power & Hot Utility Req.	10,738	-802	1,425	1,437	2,112	14,911
Fuel Energy for Electricity Generation	1,009	839	9	1,102	145	3,105
Fuel Energy for Steam/Heat Transfer Fluid	18,864	12	2,106	2,027	3,060	26,069
Auxiliary Fuel Requirements for Incineration	357	0	0	0	0	357
<i>Total Fuel Energy Required</i>	20,230	851	2,115	3,129	3,205	29,531
Fuel Energy Credit	-2,722	-1,585	0	0	0	-4,307
Net Fuel Energy Consumed in Process	17,509	-733	2,115	3,129	3,205	25,224

Level 1: Energy Requirements for the Benchmarked Heat Integration Case

The energy requirements for the PEP Benchmark Case are identical to those of the base case.

Level 2: Energy Requirements for Optimum Heat Integration

Process Stream Heat Exchangers

There are opportunities for process stream heat exchangers for the stream combinations listed below. The total fuel energy saved by these heat exchanger networks is 1384 BTU per pound of caprolactam.

- Cyclohexane oxidation section: The reboiler of the cyclohexanone column can be driven by the effluent of the oxidation reactors.
- Nitric oxide hydrogenation section: The ammonia feed can be preheated with the effluent of the converter.
- Rearrangement and purification section: The stirred kettles can be heated with the hot bottom streams of the benzene columns.
- Rearrangement and purification section and ammonium sulfate recovery section: The crystallizers can be partially heated with the product streams from the caprolactam columns and with product streams from the thin film evaporators.

Heat Pumps

A heat pump can be applied in the Cyclohexanone oximation section. The overhead stream of the cyclohexanone stripper can be compressed to supply heat to the reboiler of the same column. Resulting fuel energy savings are 1236 BTU per pound of product.

Table 31 summarizes the energy requirements for Level 2. Heat integration results in about 10% savings in total fuel required from Level 0.

Table 31. Level 2 Energy Requirements for Caprolactam Production

Optimum Heat Integration: From cyclohexane via oxidation, nitric oxide hydrogenation, cyclohexanone oximation and Beckmann rearrangement with four process stream heat exchangers and a heat pump.

Energy requirements in BTU per pound of product.

	Oxidation	Hydrogenation	Oximation	Rearrangement & Purification	NH ₃ SO ₄ Rec.	Total Process
Electricity Requirement	313	260	72	342	45	1,032
Hot Utility Requirement	11,198	0	437	1,088	1,858	14,581
Auxiliary Fuel Requirements for Incineration	357	0	0	0	0	357
Hot Utility Credit	-1,839	-1,071				-2,910
Net Power & Hot Utility Req.	10,029	-811	509	1,430	1,903	13,060
Fuel Energy for Electricity Generation	1,009	839	231	1,102	145	3,326
Fuel Energy for Steam/Heat Transfer Fluid	17,814	0	648	2,014	2,750	23,226
Auxiliary Fuel Requirements for Incineration	357	0	0	0	0	357
Total Fuel Energy Required	19,180	839	878	3,116	2,895	26,909
Fuel Energy Credit	-2,722	-1,585	0	0	0	-4,307
Net Fuel Energy Consumed in Process	16,458	-746	878	3,116	2,895	22,603

Level 3: Energy Requirements for Process Redesign

Selected Option for Level 3

The process redesign option chosen for Level 3 is in the category of *Unit Operation Design* and *Material Selection*. The production of caprolactam is complex, with many unit operations and process steps. Because of this, process modifications focused on possible substitutions for the major sections of the process.

In the caprolactam process, the Cyclohexane Oxidation Section of the process represents 70 percent of the energy requirement for the overall process. The search for redesign options was therefore focused on ways to reduce the energy consumed in this section of the process.

PEP Report 7C²⁸ describes three commercial technologies for cyclohexane oxidation. These are described below.

- The conventional process (used in the base case)--Cyclohexane is air oxidized to KA oil, and a small quantity of cyclohexyl hydroperoxide (CHHP), which is then converted to KA.
- The hydroperoxide process--Cyclohexane is oxidized primarily to CHHP, which is then converted to KA.
- The boric acid process--Cyclohexane is oxidized primarily to cyclohexylborate, which is then hydrolyzed to cyclohexanol.

Of these three routes, the hydroperoxide route is the least energy intensive. In this technology, CHHP production and decomposition take place in separate, distinct steps. The two step process minimizes oxidation by-products (via overoxidation) and controls the CHHP decomposition separately to minimize decomposition by-products (via cyclohexyloxy radicals). By controlling KA production in two steps, the hydroperoxide process generally gives higher overall KA selectivities than conventional oxidation processes.

Table 32 summarizes the energy requirements for caprolactam production using the hydroperoxide process for cyclohexane oxidation. They constitute 32% savings in total fuel energy required but 5% reduction in fuel energy credit compared to the Level 0 base case. Overall, the net fuel energy consumption is reduced by over 30% from the base case when the substitution is made.

PEP Report 7C states that the capital and operating costs for the conventional cyclohexane oxidation route and the hydroperoxide process are comparable. Capital equipment costs for the hydroperoxide process are higher, mainly due to the cost of the catalyst for the fixed bed CHHP decomposition. This increase is offset, however, by the reduced raw material and utility costs for the hydroperoxide process and the smaller, cleaner waste streams which are produced by this process and result in lower costs for waste treatment. Product values comparing this oxidation process with the conventional process were not available.

Table 32. Level 3 Energy Requirements for Caprolactam Production

Process Redesign: From cyclohexane via oxidation (hydroperoxide process), nitric oxide hydrogenation, cyclohexanone oximation and Beckman rearrangement plus four process stream heat exchangers and one heat pump.

Energy requirements in BTU per pound of product.

	Oxidation	Hydrogenation	Oximation	Rearrangement & Purification	NH ₃ SO ₄ Rec.	Total Process
Electricity Requirement	108	260	72	342	45	827
Hot Utility Requirement	5,640	0	437	1,088	1,858	9,023
Auxiliary Fuel Requirements for Incineration	204	0	0	0	0	204
Hot Utility Credit	-1,687	-1,071	0	0	0	-2,758
Net Power & Hot Utility Req.	4,265	-811	509	1,430	1,903	7,296
Fuel Energy for Electricity Generation	349	839	231	1,102	145	2,666
Fuel Energy for Steam/Heat Transfer Fluid	11,726	0	648	2,014	2,750	17,137
Auxiliary Fuel Req. for Incin.	204	0	0	0	0	204
<i>Total Fuel Energy Required</i>	12,279	839	878	3,116	2,895	20,008
Fuel Energy Credit	-2,498	-1,585	0	0	0	-4,083
Net Fuel Energy Consumed in Process	9,781	-746	878	3,116	2,895	15,925

4. OTHER METRICS

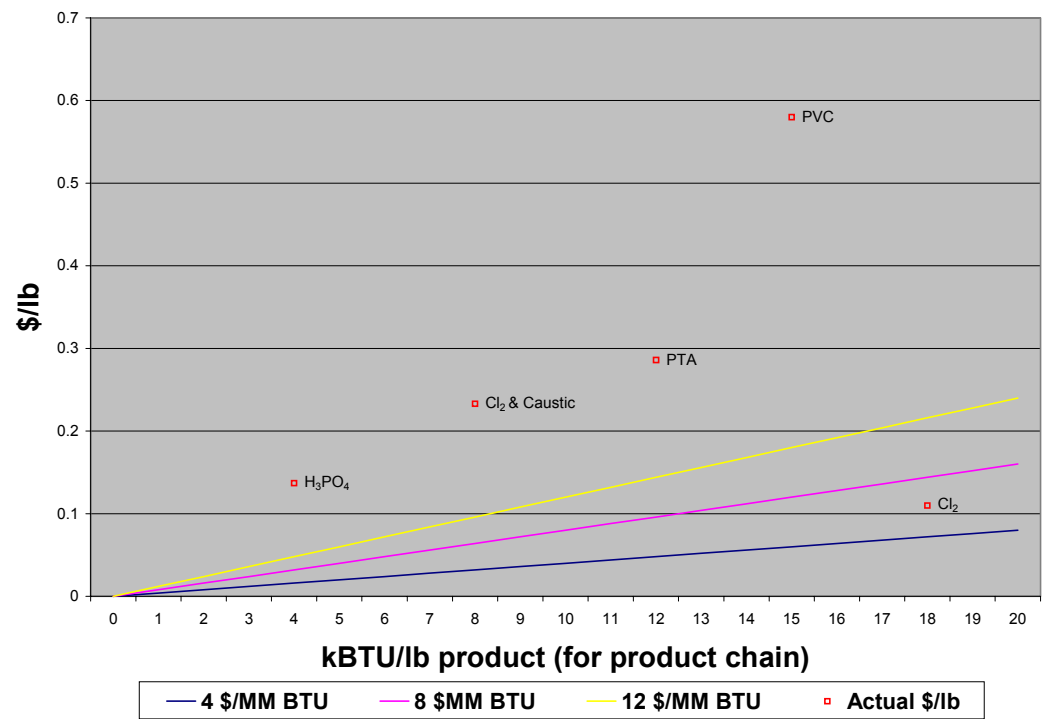
A key indicator of the sustainability of a manufacturing process is the energy consumed per unit of output. The use of energy derived from fossil fuels is often directly tied to other indicators of sustainability, such as resource consumption and toxics and other pollutants dispersed especially greenhouse gases. Energy consumption is also a critical factor in the cost of producing many products. Use of energy performance levels in management decision-making can be much more powerful if linked to other considerations, such as price and other sustainability metrics. A partial evaluation of the linkage between energy performance levels and other metrics is given below to illustrate such calculations. The parameters were primarily chosen because their values were relatively easily obtained for illustrative purposes. Other parameters may be more useful for more extensive analyses in the future.

The relationship between energy intensity and production costs, selling price, etc. can be evaluated in an attempt to identify products that would be most affected by increases in the cost of energy. Energy intensity was related to product selling price in Figure 10 to illustrate this approach. The three energy lines in Figure 10 show the cost of energy per pound of product over a range of energy requirements. Plotting typical selling prices of products on this graph gives an indication of the sensitivity of the product to the price of energy. Within this small sample of products it can be seen, for example, that phosphoric acid will be more susceptible to an increase in the cost of energy than will PVC. Also, if the caustic by-product made in the production of chlorine could not be sold, the chlorine product would bear the full energy cost burden. At an energy price of \$8 MMBTU, the selling price of chlorine alone would not be enough to cover the cost of the energy required to produce it.

Once a product has been targeted for improvement, energy performance levels and sustainability metrics can be used to evaluate alternatives for reducing its energy intensity. Energy performance levels can be used to gauge the potential for improving the energy efficiency through improvements in process design. Metrics can be used to investigate alternative raw materials or fuel sources or alternative processes for the manufacture of raw materials. Sustainability metrics can also be used in conjunction with energy performance levels to determine the relationship between energy intensity and other sustainability metrics.

Figure 1 is an example of how the sustainability metrics for energy intensity, material intensity, water consumption and greenhouse gases vary with energy performance levels for maleic anhydride. The levels show reductions in greenhouse gases and water consumption with reductions in energy intensity. The metrics for process redesign, however, indicate that the improvements in the energy metric come at the expense of an increase in material intensity. Future efforts should include development of an approach for addressing such trade-offs.

Figure 10. Selling Price of Product Compared with the Cost of Energy to Produce the Product



5. USE OF METHODOLOGY

The methodology developed in this report is one example of how a company can compare their process efficiency to calculated energy performance levels. This section discusses steps involved in such comparisons.

The first step is to define the process boundaries for the company's process. In Section 3, a block diagram and process description are given for the base case for the five processes evaluated in this study. They show, for example, whether or not waste treatment or catalyst recovery units are included in the energy requirements. The company's process boundaries should be developed using similar boundaries for comparative purposes.

The next step is to calculate the energy requirements for the company's process using the methods described in Section 2.3 and Tables 4-5. The company's energy requirements can then be compared to those given in this report.

Energy requirements can be compared most easily using *Net Power & Hot Utility Requirements*. *Net Fuel Energy Consumed*, or *Total Energy Consumed by the Process*, can also be used, as long as the energy calculations for the actual process are performed according to the formulas given in Table 5, including using the same efficiencies for steam and power generation. (If these efficiencies are not used, the comparison will be more difficult to interpret, because it will reflect differences in these efficiencies, rather than just in process performance.)

Total Energy Consumed in the Product Chain is somewhat difficult to compare, because the energy consumed in feedstock production is a "rolled up" value obtained from the life cycle analysis software, and the distinct components used in its calculation are difficult to extract. The function of this energy calculation is not so much for benchmarking, but as a criterion for evaluating the effect of a change in feedstock type on the energy intensity of the product chain.

Once a company determines where the energy efficiency of their process falls within these levels, it can begin to assess how much room for improvement exists and whether further improvement can be accomplished by increased heat integration within the existing process, or whether some type of process redesign will be required. If, for example, a company has calculated the heat and power requirements for their process, and the requirement is significantly higher than the Optimized Heat Integration (Level 2) figure, this is an indication that the potential exists for making energy reductions at fairly low cost, primarily through heat integration. If the company's process energy usage is already lower than Level 2, but higher than of Process Redesign (Level 3), there may still be options for improved energy efficiency, but changes in the process configuration will probably be required. Whether or not the cost of changing the process is practical will depend on the nature of the change and whether the company is contemplating retrofitting an existing plant or building a new facility.

The energy performance levels calculated in this report have several limitations which should be considered if a company uses them for evaluating their own processes. Some of these limitations are summarized below.

Limitations of Optimized Heat Integration (Level 2) Energy Performance Level

Significant energy savings are possible with heat integration. The literature cites that 30 to 50% energy savings, compared to conventional practice are possible even in retrofit situations.²⁹ The savings in fuel requirements achieved with heat integration for the five products considered in this project range from less than two percent for acetic acid to about 15 percent for acetic anhydride and terephthalic acid.

Although the savings resulting from heat integration are appreciable in the project results, the necessary boundaries of the project force some significant limitations to optimum heat integration. One important limitation is that the only heat sources and heat sinks that can be considered are those within the process itself. In actual practice, multiple chemical processes are usually carried out in one complex, and there are more opportunities for heat integration. The availability of additional sources of inexpensive energy from neighboring processes will result in significant reductions in fuel energy use. Thus, in some cases the energy use calculated in this study may be considerably higher than what integrated complexes are achieving for the production of these chemicals.

For this project, heat integration was also limited to identifying retrofit opportunities within each process. Heat integration is actually most effectively applied in the design phase of a process, when the total process or the total complex can be energy integrated, including the utility systems.

Limitations of Process Redesign (Level 3) Energy Performance Level

In this study, the evaluations of process redesign options were limited to process changes for the same reaction chemistry. Lack of specific data also limited the evaluations which could be performed. In order to make a valid comparison of the effects that a process change would have on the energy requirements of a process, fairly detailed information is usually required. In some cases, the information from patents and the literature was not specific enough to fully investigate the redesign options or to make reasonable estimates.

When adequate data was available, redesign options were selected or eliminated on the basis of energy use and economic practicality. The effect of the process changes on other sustainability metrics, such as pollutants and toxics dispersion and water consumption, should also be investigated in order to provide a more complete understanding of the benefits and costs of the redesign options.

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